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Jolanta KOZŁOWSKA-STRAWSKA[1]

UTILIZATION OF SELECTED PLANT INDICATORS FOR EVALUATING THE SUPPLY OF PLANTS IN SULFUR

MOŻLIWOŚĆ WYKORZYSTANIA WYBRANYCH WSKAŹNIKÓW ROŚLINNYCH W OCENIE STOPNIA ZAOPATRZENIA W SIARKĘ ROŚLIN UPRAWNYCH

Abstract: Plant indicators are often used at evaluating the level of plant's supply in nutrients. In the case of sulfur, they are: $S_{tot.}$, N:S ratio, S-SO_4 content, and total sulfur to sulfates ratio. Mainly the crop species should determine the selection of the most appropriate indicator. Therefore, the aim of present research was the assessment of a possibility to apply some plant indicators when evaluating the sulfur nutrition of crops grown under conditions of various soil acidity. The study was carried out on a base of two series of strict pot two-year experiments. The soil material was collected from the plough layer of lessive soil with granulometric composition of strong dusty sandy light loam. The experiment was established by means of complete randomization and included 2 variable factors (sulfur dose, calcium dose) at three levels. Sulfur nutrition was applied in a form of Na_2SO_4 while liming as $CaCO_3$ was used only once before experiment setting. The spring rapeseed, followed by spring barley (series I) as well as white mustard and oats (series II) were the test plants. The plant selection was determined by their nutritional needs in respect to sulfur along with their sensitivity to acidification. Results from performed experiments indicated that applied factors affected the values of indicators helpful in assessing the crop's sulfur supply level. Among studied plant indicators, sulfur nutrition caused prominent increase of total and sulfate forms of sulfur, and the increase was much higher in the case of rapeseed and white mustard. Applying Na_2SO_4 was also associated with higher abundance of sulfates as compared with total sulfur, which was reflected as the increase of S-SO_4 : S_{tot} ratio. The reliable indicator for assessing the level of crop's supply with sulfur appeared also to be N:S ratio, that was prominently lower at plants from sulfur-treated objects as compared with values recorded in dry matter of control plants (S_0).

Keywords: plant indicators, total and sulfate sulfur contents, sulfate to total sulfur ratio, N : S ratio

Introduction

Evaluating the level of crop's providing with nutrients is a very important issue from a point of view of their appropriate nutrition. Optimum crop nutrition level has positive

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[1] Department of Agricultural and Environmental Chemistry, University of Life Science in Lublin, ul. Akademicka 15, 20–950 Lublin, Poland, phone: + 48 81 445 60 18, email: jolanta.kozlowska@up.lublin.pl

effects on a yield size and quality. It is also economically and ecologically significant problem, because high fertilization efficiency can be reached under such conditions, and quantities of components transferred out of the root system, are relatively low [1, 2].

Sulfur is one of the nutrients that is necessary for a proper development of living organisms. Taking into considerations the plant's quantitative requirements for sulfur, the element is usually ranked at fourth place after nitrogen, potassium, and phosphorus [3]. It enters many important compounds, the lack of which makes disturbances of plant development and diseases at humans and animals [4, 5]. Various plant indicators are helpful at evaluating the level of plant's supply with sulfur. The most common are: S_{tot}, Nj:jS ratio, $S\text{-}SO_4$ content, and sulfates to total sulfur ratio [6, 7].

However, studies conducted in Poland indicated that the decrease of sulfur deposits from atmosphere and the decrease of the component level introduced along with mineral fertilizers led to sulfur deficiency in plant production [8, 9]. Thus, the lack of sulfur can be suspected namely on lighter – usually acidified – mineral soils localized at some distance from industrial centers [10, 11].

Therefore, the aim of present research was to assess the possibility of applying selected plant indicators for evaluating the sulfur nutrition of crops grown under conditions of various soil acidity.

Material and methods

The study consisted of two series of strict two-year pot experiments. The experiments were carried out on soil material collected from the ploughing layer of lessive soil of granulometric composition of strong dusty sandy light loam. The soil was characterized by very acidic reaction, low level of available phosphorus and sulfates, as well as very low content of available potassium and magnesium.

The experiment was established by means of complete randomization method and included two variable factors (sulfur and calcium doses) at three levels. Sulfur nutrition in a form of Na_2SO_4 and liming as $CaCO_3$ was applied only once before experiment setting in accordance with attached scheme (Table 1).

Table 1

Scheme of the experiment

	Object	Description
1	S_0Ca_0	S_0 – no sulfur nutrition
2	S_1Ca_0	S_1 – nutrition with sulfur as Na_2SO_4 at rate of 0.012 g $S \cdot kg^{-1}$ of soil
3	S_2Ca_0	S_2 – nutrition with sulfur as Na_2SO_4 at rate of 0.024 g $S \cdot kg^{-1}$ of soil
4	S_0Ca_1	Ca_0 – no liming
5	S_1Ca_1	Ca_1 – liming using calcium carbonate according to 0.5 Kh – 0.582 g $CaO \cdot kg^{-1}$ of soil
6	S_2Ca_1	Ca_2 – liming using calcium carbonate according to 1.0 Kh – 1.164 g $CaO \cdot kg^{-1}$ of soil
7	S_0Ca_2	
8	S_1Ca_2	
9	S_2Ca_2	

The experimental series I included the spring rapeseed cv. Lisonne “00”, followed by spring barley cv. Start as test crops. Series II consisted of white mustard cv. Borowska, followed by oats cv. Slawko the following year as test plants. The plant selection was determined by their nutritional needs in respect to sulfur along with their sensitivity to acidification. Plants grew in pots filled with 6 kg of soil. Plants were sown every year at the end of April at amount of 20 seeds per pot. Following the emergence, plants were thinned leaving 7 crucifer and 8 ones in the case of barley and oats, in each pot.

Constant NPKMg fertilization was applied for all experimental objects at the level consistent with crop’s nutritional requirements. Particular nutrients were introduced in forms of: N – NH_4NO_3; P – $Ca(H_2PO_4)_2 \cdot H_2O$; K – KCl; Mg – $MgCl_2 \cdot 6H_2O$. Constant moisture content at the level of 60% of the field water capacity was maintained during the vegetation season.

Every experimental plant was grown in six replicates. Plant harvest was carried out at full blossom (2 replicates) and full ripeness phase (4 replicates).

Determination of chemical properties of the soil used for experiments was made by means of methods commonly applied in chemical-agricultural laboratories. The sulfates were determined in soils samples before experiment and after crop harvest in 1st and 2nd year by means of nephelometry according to Bardsley and Lancaster’s [12]. Also pH in 1 mol KCl was measured in the soil material using glass electrode (potentiometry).

After the plant harvest at blossom phase, plant material was digested in concentrated sulfuric acid with addition of H_2O_2 and then total nitrogen was determined by means of Kjeldahl method.

When plant material was extracted using 2% CH_2COOH with active coal addition, sulfates were determined nephelometrically [13]. Total sulfur was determined applying Butters-Chenery method [14].

All analyses of soil and plant material were done in two replicates of averaged object samples. Attached tables present mean values.

After the plant harvest at full ripeness phase, statistical evaluation of yields (seeds, straw) was performed. The evaluation was made by means of variance analysis for factorial experiments using Tukey confidence intervals.

Results and discussion

Plant indicators are often used at evaluating the level of plant’s providing with nutrients. In the case of sulfur, they are: S_{tot}, N:S ratio, S-SO_4 content, and sulfates to total sulfur ratio. [3, 6, 7, 15–18]. It is difficult to univocally find, which of them is the best. Some authors underline [19] that mainly the crop species, for which the level of sulfur supply is being assessed, should determine the selection of the most appropriate indicator.

The most common sulfur-supply indicators were determined for test plants harvested at blossom phase (Table 2). This can allow for possibly quick intervention in the case of any sulfur deficit during crop production and reduce damages associated with lower yields and their worse quality [3, 15, 20].

Table 2

Influence of sulfur nutrition and liming on selected indicators expressing the sulfur supply of crops harvested at blossom phase

Object	S_{tot} [$g \cdot kg^{-1}$]	S-SO_4 [$g \cdot kg^{-1}$]	S-SO_4 : S_{tot}	N_{tot} : S_{tot}
Spring rapeseed				
S_0Ca_0	4.5	2.0	0.44	13.8
S_1Ca_0	8.3	2.5	0.30	7.5
S_2Ca_0	11.5	4.0	0.35	5.7
S_0Ca_1	2.5	1.0	0.40	11.9
S_1Ca_1	5.0	2.4	0.48	5.3
S_2Ca_1	6.3	3.6	0.57	4.2
S_0Ca_2	2.3	0.9	0.39	10.8
S_1Ca_2	4.8	2.0	0.42	5.6
S_2Ca_2	6.1	3.2	0.52	4.9
Spring barley				
S_0Ca_0	2.7	1.2	0.44	16.1
S_1Ca_0	3.3	1.7	0.52	14.0
S_2Ca_0	3.8	2.1	0.55	10.6
S_0Ca_1	2.5	1.2	0.48	15.7
S_1Ca_1	2.8	1.4	0.50	11.9
S_2Ca_1	3.2	1.7	0.53	10.7
S_0Ca_2	1.6	0.9	0.56	19.1
S_1Ca_2	1.9	1.1	0.58	16.1
S_2Ca_2	2.1	1.3	0.62	13.7
White mustard				
S_0Ca_0	7.8	2.6	0.33	X
S_1Ca_0	9.3	3.5	0.38	X
S_2Ca_0	10.0	3.6	0.36	X
S_0Ca_1	4.1	0.5	0.12	8.6
S_1Ca_1	6.4	1.5	0.23	5.2
S_2Ca_1	8.8	3.1	0.35	4.2
S_0Ca_2	4.5	0.8	0.18	8.7
S_1Ca_2	6.5	1.9	0.29	5.9
S_2Ca_2	7.6	2.9	0.38	4.2
Oats				
S_0Ca_0	2.3	1.1	0.48	14.7
S_1Ca_0	3.0	1.6	0.53	11.9
S_2Ca_0	3.7	2.1	0.57	9.5
S_0Ca_1	1.6	0.8	0.50	17.7
S_1Ca_1	1.6	0.8	0.50	17.4
S_2Ca_1	2.4	1.4	0.58	11.8
S_0Ca_2	1.7	0.9	0.53	16.8
S_1Ca_2	1.8	1.0	0.56	15.4
S_2Ca_2	2.3	1.4	0.61	12.6

X – not determined due to lack of material.

For spring rapeseed harvested at blossom phase, the quantity of total sulfur in plant dry matter oscillated within quite wide range (2.3–11.5) g · kg^{-1}. Plants from control objects (S_0Ca_0, S_0Ca_1, S_0Ca_2), to which sulfur nutrition was not applied, were characterized by the lowest content of discussed sulfur form. Nevertheless, when comparing the total sulfur in analyzed objects, it is prominent that levels of this sulfur form at plants from S_0Ca_0 object is almost twice as high as those found in S_0Ca_1 and S_0Ca_2 objects. It probably results from the "component's concentrating effect", since plants could not find any beneficial conditions for growth and development in analyzed object. Such conclusion could be confirmed by the yield size of plants harvested at full ripeness phase (Table 3). Crops from here discussed object produced the lowest seed and straw yields.

Table 3

Influence of sulfur nutrition and liming of soil acidity [pH_{KCl}]

Soil	Object								
	Ca_0			Ca_1			Ca_2		
	S_0	S_1	S_2	S_0	S_1	S_2	S_0	S_1	S_2
After rapeseed harvest – blossom phase	4.3	4.3	4.3	4.9	5.2	5.0	6.1	5.9	5.9
After barley harvest – blossom phase	4.2	4.6	4.5	4.7	4.9	4.2	5.4	5.4	5.1
After mustard harvest – blossom phase	4.5	4.4	4.4	5.4	5.2	5.3	6.4	6.5	6.3
After oats harvest – blossom phase	4.2	4.3	4.1	4.9	4.9	5.0	5.8	5.7	5.7
After rapeseed harvest – full ripeness phase	4.1	4.2	4.1	4.7	4.8	4.7	5.8	5.8	5.8
After barley harvest – full ripeness phase	3.9	3.8	3.8	4.0	4.1	4.1	5.6	5.6	5.7
After mustard harvest – full ripeness phase	4.1	4.1	4.1	4.9	5.1	4.9	6.2	6.3	6.1
After oats harvest – full ripeness phase	4.1	4.1	4.1	4.5	4.6	4.6	5.7	5.7	5.6
Before experiment	3.85								

Unlike control objects, the lowest total sulfur content characterized crops grown with sulfur addition at the rates of 0.012 gS · kg^{-1} and 0.024 gS · kg^{-1} of soil, although soil acidification associated with lack of liming (Ca_0) was the factor that limited the yield size (Table 3). In analyzed objects, total sulfur level due to "component concentrating effect" [21] amounted (8.3–11.5) g · kg^{-1}. It is often underlined in numerous literature references that besides fertilization using various nutrients, liming greatly determines the amount of produced biomass during cultivation of crops, namely those sensitive to low pH [22].

In the case of objects, where liming was done, a clear dependence between total sulfur and seed and straw yields of spring rapeseed can be observed (Table 4). The increase of sulfur dose applied was accompanied by the increase of total sulfur amount determined in dry matter of plants harvested at blossom phase and the increase of yield size of generative and vegetative parts of analyzed crop. Numerous studies upon the impact of nutrition on quality and size of yields for crops often underlined that there is some regularity indicating that plants utilize nutrients more effectively when they are applied in proportions adjusted to crop's nutritional requirements [23]. Referring to spring rapeseed as a plant species particularly sensitive to sulfur deficits in an environment, higher sodium sulfate (0.024 gS · kg^{-1} of soil) appeared to be the most appropriate.

Table 4

Influence of sulfur nutrition and liming on crop yielding [g d.m. · pot^{-1}]

Crop Object	Series I				Series II			
	Spring rapeseed		Spring barley		White mustard		Oats	
	Seeds	Straw	Grain	Straw	Seeds	Straw	Grain	Straw
S_0Ca_0	0.62	9.32	b.n.	1.61	b.n.	0.31	18.21	23.30
S_1Ca_0	1.79	16.80	b.n.	1.73	b.n.	0.64	18.98	24.05
S_2Ca_0	2.39	24.85	b.n.	1.94	b.n.	1.04	20.31	24.99
S_0Ca_1	1.29	54.12	4.80	11.34	6.99	39.15	20.20	25.40
S_1Ca_1	18.33	63.25	10.37	16.40	9.62	41.65	20.80	26.86
S_2Ca_1	22.55	65.10	13.58	17.71	9.82	41.57	20.92	26.87
S_0Ca_2	2.11	80.45	19.86	29.51	10.19	46.95	22.64	28.79
S_1Ca_2	25.42	83.57	23.65	29.52	10.81	47.92	25.82	30.41
S_2Ca_2	35.46	91.15	25.65	33.14	11.19	49.95	28.21	30.45
LSD ($p = 0.01$)								
S	0.71	2.27	1.36	1.19	0.42	1.15	1.24	1.34
Ca	0.71	2.27	1.06	1.19	0.33	1.15	1.24	1.34
S · Ca	1.34	4.33	1.54*	2.26	0.66	2.19	2.35	n.i.

* – differences significant only at the level of $p = 0.05$; b.n. – lack of material; n.i. – insignificant differences.

Changes in total sulfur content in dry matter of spring rapeseed harvested at blossom phase were also accompanied by alterations of S-SO_4 level. Like for total sulfur, the highest sulfate concentration was recorded at plants from objects, where liming was given up. Due to unfavorable conditions for growth and development, crops produced much lower seed and straw yields.

Plants from series limed according to 1.0 HA (hydrolitic acidity) were characterized by the lowest sulfate content, which was reflected in the amount of sulfates recorded in the soil after the plant harvest (Table 5) as well as seed and straw yields determined after rapeseed harvest at full ripeness phase (Table 4).

Applying the sodium sulfate also contributed to changes of S-SO_4 to S_{tot} proportions in spring rapeseed dry matter. Sulfur nutrition caused the increase of this ratio in limed objects. Better plant providing with sulfur usually makes the decrease of the component incorporation within organic compounds [24], while on the other hand, higher sulfate contents in crop's biomass means that they were insufficiently provided with sulfur [25].

The N : S ratio in dry matter of rapeseed harvested at blossom phase ranged within 4.2–13.8. Some authors underline that this indicator is better for assessing the level of plant's supply with sulfur rather than total sulfur and sulfates concentrations [19]. Under conditions of present experiment, the N : S ratio reached the highest values in objects, where sulfur nutrition was not applied at all. Nitrogen to sulfur ratio is somehow disturbed at sulfur deficiency, which in consequence may diminish the nitrogen utilization and leading to lower size and quality of crop's yields [22]. In the case of spring rapeseed, plants produced the lowest seed and straw yields at N : S ratio of 10.8–13.8, which may indicate that sulfur deficit could be the factor that limited the yielding.

Table 5

Influence of sulfur nutrition and liming on sulfates content in the soil [mg · kg^{-1}]

Soil	Object								
	Ca_0			Ca_1			Ca_2		
	S_0	S_1	S_2	S_0	S_1	S_2	S_0	S_1	S_2
After rapeseed harvest – blossom phase	17.0	27.8	26.6	11.2	9.0	8.3	4.8	7.4	10.4
After barley harvest – blossom phase	19.6	28.4	37.6	19.2	25.0	22.0	17.6	24.3	24.1
After mustard harvest – blossom phase	21.8	25.4	49.9	11.6	7.9	15.4	4.8	4.7	10.4
After oats harvest – blossom phase	22.2	28.8	36.0	24.7	22.5	28.0	26.4	27.4	23.6
Before experiment	19.7								

Objects treated with sulfur at the level of S_2 revealed the N : S ratio 1.2–1.3-fold lower as compared to values recorded after sulfur nutrition at S_1 rate. Higher rapeseed seed and straw yields were the effects of better crop supply with sulfur, namely in limed objects. It is also confirmed by literature data [3, 19, 26] pointing out that the N:S value is quite good indicator of rapeseed providing with sulfur.

In the case of spring barley, that is a plant species with relatively modest nutritional requirements in respect to sulfur [23, 27], the level of the element supply might determine the size and quality of yields, because appropriate crop providing with sulfur has beneficial influence on photosynthesis, protein biosynthesis, and nucleic acids contents, and in consequence, necessary technological value of yield [22].

Contents of S_{tot} and S-SO_4 in spring barley dry matter harvested at blossom phase prominently depended both on sulfur nutrition level and soil acidification (Table 3). Plants from objects where liming was not applied (Ca_0) were characterized by the highest concentration of analyzed sulfur forms. In those objects, quantity of total sulfur was at the level of 2.7–3.8 g · kg^{-1}, while that of sulfates 1.2–2.1 g · kg^{-1}. Such large amount of sulfur may be attributed to the "component concentrating effect", which was reflected by barley grain and straw yields harvested at full ripeness phase. Crops produced minimum grain yields and low (1.61–1.94 g · pot^{-1}) straw yield in objects, where liming was not done. Also the concentration of sulfates left in the soil after the crop harvest (Table 5) may indicate that mainly soil acidification was the factor limiting the plant yielding in objects without liming (Ca_0) (Table 3). It is frequently emphasized that sulfur availability for plants greatly depends on the soil acidity. Alkaline reaction of the soil accelerates the organic matter decomposition and sulfur release, whereas low pH values intensify the sulfates adsorption on hydrated iron and aluminum oxides, as well as kaolinite, which reduces the sulfur availability for plants [28].

The S-SO_4 : S_{tot} ratio is also worth mentioning among discussed indicators of spring barley providing with sulfur. Studies conducted upon the sulfur utilization level by crops [19] revealed that sulfate to total sulfur ratio is quite constant during the whole vegetation season and is more suitable for assessing the plant supply with sulfur than total sulfur or sulfates concentration.

When comparing value of S-SO_4 : S_{tot} in dry matter of barley harvested at blossom phase, it is noticeable that sodium sulfate application resulted in relatively larger increase of sulfates than organic sulfur contents. It was proven by the increase of S-SO_4 : S_{tot}, namely in objects, where sulfur was introduced at the amount of 0.024 gS · kg^{-1} of soil. It was probably due to the fact that better plant supply with sulfur causes that those plants incorporate that nutrient into organic compounds to a lesser degree [24, 25]. In addition, increased sulfates content in plant biomass means that crops were sufficiently provided with the element, which was confirmed by presented pot experiment. Value of S-SO_4 : S_{tot} ratio in dry matter of barley from objects treated with sulfur was about 1.1–1.3-fold higher in reference to levels recorded at plants, to which sulfur was not introduced. Better supply of these plants with sulfur resulted also in the increase of grain and straw yields observed after the barley harvest at full ripeness phase.

Ratio N:S also seems to be a reliable indicator of spring barley providing with sulfur. Literature references underline that the ratio should amount to 17 : 1 at optimum grasses supply with sulfur. For spring barley harvested at blossom phase, that value oscillated around 10.6–19.1. Some prominent decrease of N:S ratio was recorded for plants, to which sulfur nutrition was applied. It was probably associated with the influence of sodium sulfate on total sulfur content increase and decrease of total nitrogen concentration at plants from those objects. Perhaps, sulfur treatment improved crop providing with the nutrient [19], which in turn affected the increase of barley grain and straw yields determined at full ripeness phase.

White mustard – as similar as spring rapeseed – is a plant species with particularly large nutritional requirements for sulfur. The plant produces specific sulfur compounds (fatty acids, bitter oils, etc.), its utility value depends on [29, 30].

When considering the influence of sodium sulfate nutrition on total sulfur and sulfate concentrations in dry matter of white mustard harvested at blossom phase, it can be observed that plants from objects without liming were characterized by the highest contents of analyzed sulfur forms. It was probably associated with the “component concentrating effect” and was also reflected in seed and straw yield size determined after mustard harvest at full ripeness phase (Table 4). In objects of series Ca_0 (no liming), plants did not produce seeds at all. Quantity of sulfates found in the soil under series Ca_0 determined after white harvest at blossom phase (Table 5) may suggest that the plant species strongly reacted towards low soil pH (Table 3) and did not utilize available sulfur forms in full. It is somehow surprising reaction, since white mustard is considered as a plant of light soils, thus not counted to particularly sensitive to soil acidification [30].

At plants from analyzed objects, amount of total sulfur was at the level of (7.8–10.0) g · kg^{-1}, which about 1.1–1.9-fold exceeded total sulfur content found at crops of series with liming according to 0.5 Kh (Ca_1) and 1.3–1.7-fold in reference to plants of series Ca_2. It was more obvious in the case of sulfates, for which their amount was 1.2–5.2

times higher in dry matter of plants of series Ca_0 as compared with values recorded at plants of series Ca_1 and 1.2–3.3 times higher in relation to series Ca_2.

Comparing both above indictors that describe the mustard supply with sulfur with sulfur to total sulfur ratio, it is prominent that also plants of series Ca_0 were characterized by the highest values of the proportion. In analyzed objects, the $S\text{-}SO_4 : S_{tot}$ was at the level of 0.33–0.36, which was 1.3–2.8-fold higher as compared with data recorded at plants from other objects. High values of the proportion may indicate that besides sulfur nutrition of the test crop, also soil liming might play some important role. When the soil is of improper acidity, nutrients are worse utilized by plants and their uptake is often disturbed. Not only the yields of generative parts is decreased then, but its technological value is worsened as well [20, 22].

However, it is worth underlining that in the case of majority of objects, namely those of series Ca_1 and Ca_2, the increase of sodium sulfate dose caused obvious increase in $S\text{-}SO_4$ to S_{tot} value of white mustard dry matter, which may indicate that the crop utilized sulfur better from directly available forms. It is reflected in the amount of sulfates found in the soil of these objects, analyzed when mustard was harvested at blossom phase (Table 5).

The total nitrogen to total sulfur ratio, that is frequently used for evaluating the crop providing with sulfur, appeared to be the least reliable indicator in the case of white mustard harvested at blossom phase. Its value oscillated within 4.2–8.6 for plants of series Ca_1 and around 4.2–8.7 of dry matter of mustard from objects, where liming was applied according to 1.0 Kh.

Oat was another crop subject to evaluate the level of supply with sulfur. The species is from the plant group with relatively low nutritional requirements for sulfur; nevertheless, it is often emphasized that the requirements and reaction towards sulfur addition into the environment can increase at higher levels of nutrition using other nutrients, namely nitrogen and phosphorus [31].

Plants from series Ca_0 were characterized by the highest concentrations of total sulfur and sulfates. Dry matter of plants from above objects contained 1.4–1.9-fold more total sulfur than those of series Ca_1 and 1.4–1.7-fold more as compared with plants growing after liming according to 1.0 Kh (Ca_2). Similar situation was observed in the case of sulfates, the quantity of which at plants of series Ca_0 was 1.2–2 times higher as compared with the contents recorded in dry matter of oats from other experimental objects. It is worth noticing that sodium sulfate application caused slightly larger increase of sulfate in relation to organic sulfur content, which was confirmed by the increase of $S\text{-}SO_4 : S_{tot}$ value. The increase of sulfate content in plant biomass may indicate that they were sufficiently provided with sulfur [25].

The highest value of $S\text{-}SO_4 : S_{tot}$ ratio was recorded for oat biomass from objects, where liming was applied in accordance to 1.0 Kh. In these objects, the value was at the level of 0.53–0.61, which was 1.1-fold higher than for plants of series Ca_1 and Ca_0. It was also confirmed by the biomass of plants produced after oats harvest at full ripeness, because in series Ca_2, the crops produced significantly higher grain and straw yields.

The N:S ratio also seems to be quite good indicator of oat supply with sulfur. It is often underlined in literature references that total sulfur content may decrease during the plant's growth and development, hence the N:S ratio should be the most proposed indicator taken into consideration at evaluating the grass providing with sulfur [16].

Under conditions of presented pot experiment, value of N:S ratio ranged within 9.5–16.8. Both at plants from limed series, as well as series Ca_0, prominently lower levels of N : S ratio were recorded at plants treated with higher sulfur dose (S_2). It may indicate the high degree of sulfur from sources that were directly available for crops and finds its reflection in grain and straw yields of oats harvested at full ripeness phase. In analyzed objects, namely series Ca_2, plants produced considerably higher yields of vegetative and generative parts as compared with oats fertilized with higher sulfur rate as well as to those from control series (S_0). High value of N : S ratio in objects with no sulfur treatment, may suggest sulfur deficit within oats environment. Despite of the fact that oat is a species with relatively low sulfur requirements, the N:S ratio can be disturbed at sulfur deficits and nitrogen excess. In consequence, it leads to lower nitrogen utilization and may contribute to the decrease of plant's size and quality of yields [22].

Conclusions

Results from studies aiming at evaluating the possibilities of utilization of some plant indicators taken into consideration during evaluating the level of crop's providing with sulfur under various soil acidity, allow for drawing following conclusions:

1. Applied experimental factors exerted significant influence on values of analyzed indicators for evaluating the level of test crop's supply with sulfur.
2. Sulfur nutrition cause the increase of total sulfur and sulfate contents in dry matter of test plants. The increase was much higher in the case of rapeseed and white mustard, *ie* crops with high requirements for the component. It might indicate that these plants reacted towards sulfur deficiency within their growth environment the most clearly.
3. Unlike sulfur nutrition, calcium carbonate applying affected the decrease of analyzed sulfur forms concentration in biomass of all test crops.
4. Application of sodium sulfate also contributed to higher increase of sulfates in relation to total sulfur, which was proved by value of $S\text{-}SO_4 : S_{tot}$ ratio, and it means that test plant species were sufficiently provided with sulfur.
5. The N:S ratio also appeared to be quite good indicator of plant's supply with sulfur. As an effect of sulfur nutrition, that value was prominently lower as compared with values found at plants from the control series, which indicates that crops treated with sulfur were better provided with the nutrient.
6. Results from presented studies allow for concluding that every analyzed indicator may be used to evaluate the level of crop's supply with sulfur, and the selection of the best one should be determined mainly by the species of cultivated crop.

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MOŻLIWOŚĆ WYKORZYSTANIA WYBRANYCH WSKAŹNIKÓW ROŚLINNYCH W OCENIE STOPNIA ZAOPATRZENIA W SIARKĘ ROŚLIN UPRAWNYCH

Katedra Chemii Rolnej i Środowiskowej
Uniwersytet Przyrodniczy w Lublinie

Abstract: Przy ocenie stopnia zaopatrzenia roślin w składniki pokarmowe często wykorzystywane są wskaźniki roślinne. W przypadku siarki jest to: zawartość S ogółem, stosunek N:S, zawartość S-SO_4 oraz stosunek siarczanów do siarki ogółem. O wyborze najbardziej właściwego wskaźnika powinien w pierwszej kolejności decydować gatunek uprawianej rośliny. Stąd celem podjętych badań była próba oceny możliwości wykorzystania niektórych wskaźników roślinnych w ocenie stopnia odżywienia siarką roślin, uprawianych w warunkach zróżnicowanego odczynu gleby. Badania wykonano na podstawie dwóch serii ścisłych, dwuletnich doświadczeń wazonowych. Materiał glebowy pobrano z warstwy ornej gleby płowej o składzie granulometrycznym gliny lekkiej silnie spiaszczonej pylastej. Doświadczenie założono metodą kompletnej randomizacji i obejmowało ono 2 zmienne czynniki (dawka siarki, dawka wapna) na trzech poziomach. Nawożenie siarką w formie Na_2SO_4 i wapnowanie w postaci $CaCO_3$ zastosowano jednorazowo przed założeniem doświadczenia. Roślinami testowymi był rzepak jary, a po nim jęczmień jary (I seria doświadczalna) oraz gorczyca biała i owies (II seria doświadczalna). Przy doborze roślin brano pod uwagę ich potrzeby pokarmowe w stosunku do siarki oraz wrażliwość na zakwaszenie. Wyniki przeprowadzonych badań wskazują, że zastosowane czynniki doświadczalne wpływały na wartość wskaźników oceniających stan zaopatrzenia roślin w siarkę. Wśród rozpatrywanych wskaźników roślinnych, nawożenie siarką powodowało wyraźny wzrost zawartości siarki ogółem oraz siarczanowej, przy czym wzrost ten był znacznie wyższy w przypadku rzepaku i gorczycy. Aplikacja Na_2SO_4 wiązała się również z większym przyrostem ilości siarczanów w stosunku do siarki ogółem, co znalazło odzwierciedlenie we wzroście wartości proporcji S-SO_4 : $S_{og.}$. Miarodajnym wskaźnikiem, oceniającym stan zaopatrzenia roślin w siarkę, okazał się również stosunek N : S, który w roślinach z obiektów nawożonych siarką był wyraźnie mniejszy w porównaniu z wartościami stwierdzonymi w suchej masie roślin z serii kontrolnej (S_0).

Słowa kluczowe: wskaźniki roślinne, zawartość siarki ogółem i siarczanowej, stosunek siarczanów do siarki ogółem, stosunek N : S

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Zdzisław CIEĆKO[1], Andrzej Cezary ŻOŁNOWSKI
and Aneta MIERZEJEWSKA

IMPACT OF FOLIAR NITROGEN AND MAGNESIUM FERTILIZATION ON CONCENTRATION OF CHLOROPHYLL IN POTATO LEAVES

ODDZIAŁYWANIE DOLISTNEGO NAWOŻENIA AZOTEM I MAGNEZEM NA ZAWARTOŚĆ CHLOROFILU W LIŚCIACH ZIEMNIAKA

Abstract: The objective of the study has been to determine the effect of foliar nitrogen and magnesium fertilization on modifications in the concentration of chlorophyll in leaves of an medium-early edible potato cultivar called Zebra. Different rates of foliar magnesium fertilization were applied, from 0 % to 50 % of the full dose of this nutrient (80 kgN · ha^{-1}). The experiment was conducted in three series – without magnesium fertilization, with magnesium applied to soil (24 kgMg · ha^{-1}) and with magnesium sprayed over leaves (12 kgMg · ha^{-1}). The highest concentration of chlorophyll *a* and *b* was obtained in 2005: 137.6 and 53.4 mg · 100 g of fresh mass of leaves. In the same year, the highest yield of potato tubers was produced: on average, 27.86 Mg · ha^{-1}. This relationship, however, was not confirmed in the subsequent years. In 2006 and 2007, the two years with the weather conditions unfavourable to potato cultivation, the volume of yields was positively correlated with the concentration of chlorophyll in leaves, a relationship which was not detected in 2005, when the yield was the highest. Soil or foliar application of magnesium determined the synthesis of chlorophyll and accumulation of yield, especially in the years characterized by unfavourable weather conditions.

Keywords: chlorophyll, mineral fertilizers, magnesium, nitrogen, tuber yield, *Solanum tuberosum*, potato

Introduction

Natural pigments present in green plants are mainly magnesium-containing chlorophyll *a* (bluish green), which is the major photoreceptor, and chlorophyll *b* (greenish yellow), whose concentration in leaves is about 2- to 4-fold lower. The other pigments are pheophytin and carotenoids. Chlorophyll *a* and *b* differ in the substituent group at the third carbon atom (Chl *a* -CH_3, Chl *b* -CHO) in the porphyrin ring, which has an atom of magnesium in its centre. Among the factors which affect the rate of chlorophyll synthesis are sunlight exposure and intensity [1, 2], and among such agronomic

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[1] Department of Environmental Chemistry, University of Warmia and Mazury in Olsztyn, pl. Łódzki 4, 10–727 Olsztyn, Poland, phone: +48 89 523 35 47, email: zdzislaw.ciecko@uwm.edu.pl

treatments the most important ones are nitrogen [3] and magnesium fertilization [4, 5]. By measuring the concentration of chlorophyll in leaves, it is possible to assess the plant's photosynthetic capability [6]. The potato is a plant which is capable of producing very high yields. The yields obtained in European countries (Belgium, the Netherlands, France) reaching 40–50 Mg tubers $\cdot$ ha^{-1} require high and adequately balanced fertilization, which will first of all affect the growth of aerial parts, including the assimilating leaf area, expressed by the *leaf green area* (LAI) or the *green area index* (GAI), as well as synthesis of the plant pigments in leaves responsible for the course of photosynthesis [5]. Concentrations of these pigments determine the rate of accumulation of assimilates in storage organs of plants [3]. The development of plant aerial mass responsible for photosynthesis is distinctly affected by high availability of nitrogen (N), which in turn ensures a high yield of tubers [7]. Potato plants respond very dynamically to nitrogen fertilization by raising the concentration of chlorophyll in leaves and the effects of nitrogen application are observable in just 36 hours afterwards – especially in the case of young and fast growing potato plants [8]. According to Wierzejska-Bujakowska [9], when growing edible potato, nitrogen should be introduced together with the other nutrients in the following ratio: N:P:K as 1.0:0.4:1.3. When nitrogen is not adequately balanced, the quality of harvested tubers suffers [10]. An excessively high share of nitrogen versus the other elements leads to the formation of a large aerial mass but the tubers are often not fully mature, have a low proper mass, contain low levels of complex compounds, such as storage starch, protein, polyphenolic substances, citric acid and vitamin C, but are too rich in simple sugars, free amino acids and mineral nitrogen [11, 12]. Under elevated N fertilization, the tuber formation process can be restricted [13, 14]. Apart from nitrogen, magnesium is another element which plays an important role in potato nutrition [5, 15]. Magnesium is taken up by plants during their later vegetative growth and therefore they need additional, foliar application of this nutrient. Recommended forms of magnesium for foliar treatments are magnesium sulphate heptahydrate in a concentration of 5 %, and magnesium sulphate monohydrate in a concentration of 2–3 %, which is recommended to be used together with an aqueous solution of urea [16–19].

In the presented experiment discussed the effect of foliar and soil nitrogen and magnesium fertilization has been tested with respect to concentrations of chlorophyll *a*, *b* and sum of chlorophyll *a+b* in leaves of cv. Zebra potato. The relationships between the applied fertilization variants and concentrations of particular forms of chlorophyll as well as potato yields have also been analyzed.

Material and methods

The results originate from a three-year field experiment, set up at the Experimental Station in Tomaszkowo near Olsztyn (53°42′35″ N, 20°26′01″ E) in 2005. The experiment was established on proper brown soil developed from weak loamy sand class IVb in the Polish soil valuation system, classified as good rye complex. According to the FAO/WRB (*World Reference Base for Soil Resources*) [20], this soil belonged to Cambisols – Brown Soils. The effect of foliar nitrogen fertilization combined with foliar and soil magnesium fertilization on concentrations of chlorophyll in leaves of a medium-

-early potato cultivar Zebra (*Plant Breeding Station in Szyldak, Ltd.*) was examined. The study involved a two-factor experiment in random blocks with four replications, including different nitrogen and magnesium fertilization variants, either applied to soil or sprayed over leaves. The experiment consisted of three series: in the first one, nitrogen fertilization alone was applied in a rate of 80 kgN $\cdot$ ha^{-1}, with a gradually increasing share of foliar nutrition (0, 10 %, 20 %, 30 %, 40 %, 50 %) at the expense of soil fertilization, which equalled 80, 72, 64, 56, 48 and 40 kgN $\cdot$ ha^{-1}; the other two series included additional magnesium fertilization. In the second series, magnesium was introduced to soil in a rate of 24 kgMg $\cdot$ ha^{-1} and in the third one, it was sprayed over leaves in an amount of 12 kgMg $\cdot$ ha^{-1}. Phosphorus and potassium fertilization rates were constant in all the treatments and equalled 35 kgP and 100 kgK $\cdot$ ha^{-1}. The phosphorus fertilizer, granular triple superphosphate 20 % P ($Ca(H_2PO_4)_2$) and the potassium one, potassium salt 50 % K (KCl) were applied in a single dose to soil before planting potatoes. Nitrogen was used as urea 46 % N ($CO(NH_2)_2$), and magnesium in the form of magnesium sulphate ($MgSO_4 \cdot 7H_2O$). Whole amounts of the fertilizers introduced to soil were applied before planting potatoes, and the ones used for foliar fertilization were sprayed in five doses during the plants' vegetative season. The first spraying treatment was performed after the rows of potato plants became compact and the first flower buds formed. The subsequent treatments were carried out in 7-day intervals. The working concentration of the solutions of fertilizers applied to leaves was 6.9 % of urea and 10.0 % of magnesium sulphate. The rows were spaced at 62.5 cm and the distance between planted potatoes in a row was 40 cm. Thus, the calculated plant density was 40 thousand plants per ha^{-1}. The area of plots for harvest was 12.96 m^2. The yields obtained from the plots after harvest were recalculated and expressed as Mg tubers $\cdot$ ha^{-1}.

Samples of leaves for analyses of the content of chlorophyll were taken from the 2nd and 3rd tier in the apical part of a potato plant. The content of chlorophyll *a*, *b* and sum of chlorophyll *a+b* was determined with the colorimetric method using 80 % acetone solution as an extractant (POCh Gliwice) [21]. Leaf blades were cut into minute fragments and 1.0 g samples were taken from the green mass thus obtained. The samples were placed in tubes, to which 80 % acetone solution was poured. After 12-h maceration at 4 °C, the content of each tube was homogenized, quantitatively transferred onto a Schott #G3 funnel and filtered under partial vacuum, rinsing with 80 % acetone. The filtrate was filled up to 100 cm^3 and thoroughly mixed, after which the absorbance was measured at the wavelengths of λ = 645 and 663 nm versus 80 % acetone solution as a zero sample. The calculations included the equation proposed by Arnon [22], which is applied to colorimetric determination of concentrations of plant pigments [21, 23]. The coefficients specific for particular wavelengths were adopted from Mackinney's work [24].

$$\text{Chl } a = 12.0 \cdot A_{663} - 2.69 \cdot A_{645} \quad [\text{mgChl} \cdot \text{dm}^{-1}]$$

$$\text{Chl } b = 22.90 \cdot A_{645} - 4.68 \cdot A_{663}$$

$$\text{Chl } a{+}b = 20.20 \cdot A_{645} + 8.02 \cdot A_{663}$$

The absorbance of the assayed chlorophyll solutions was determined in a 1 cm path length quartz cuvette flow spectrophotometer type Specol 220 (Carl Zeiss Jena). The content of chlorophyll expressed in mg dm^{-3} of extract was converted into mg 100 g^{-1} of fresh mass of leaf tissue.

The results were processed statistically with ANOVA at the level of significance of $\alpha = 0.05$, using a Statistica v. 9.0 software package [25]. The correlation between the analyzed factors was established using a simple correlation coefficient, with the Microsoft Excel programme [26].

Results and discussion

Chlorophyll is a plant pigment, whose content in a plant depends on several factors. They range from agronomic treatments, *eg* applied fertilization, to environmental conditions. The rate of chlorophyll synthesis can be limited, for instance, by water deficit in soil [27], high and low temperatures [28, 29], salinity [30] and light intensity [1, 2]. The results discussed in this paper concerning the content of chlorophyll in potato leaves demonstrate a high degree of variation between the years. Such high changeability in the content of chlorophyll under the influence of the weather occurring during potato cultivation has also been suggested by Wyszkowski [31]. In the three years of the experiment, the temperature, air humidity and soil moisture which prevailed in 2005 (Fig. 1) resulted in the highest concentration of chlorophyll *a* (Chl *a*) 137.6; chlorophyll b (Chl *b*) 53.4 and the sum of chlorophyll *a*+*b* (Chl *a*+*b*) 191.0 mg · 100 g^{-1} of *fresh mass* of leaves (FM) (Table 1). The high levels of chlorophyll in leaves sampled from potato plants grown in 2005 coincided with the highest tuber yields, on average 27.86 Mg tubers · ha^{-1}. The year 2005 proved to be very favourable for potato cultivation in terms of the temperatures and precipitation, which was reflected by high

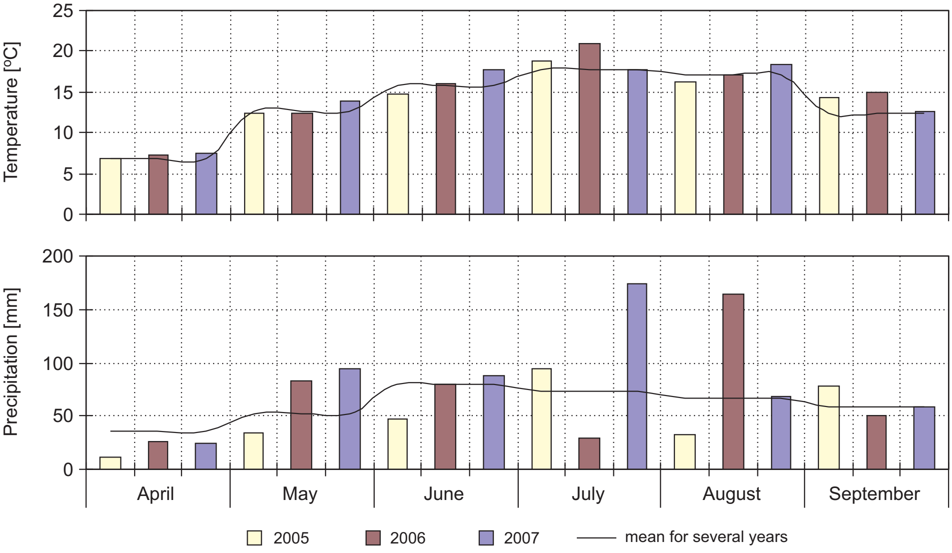

Fig. 1. Temperatures and precipitation during the vegetative growth of potatoes at the Experimental Station in Tomaszkowo

Table 1

Effect of foliar nitrogen fertilization and two magnesium fertilization technologies on the content of chlorophyll in leaves of cv. Zebra potato [mg · 100 g^{-1} fresh mass]

Treatments			2005			2006			2007			Mean 2005–2007		
NPK fertilization to the soil	foliar N fertilization	Mg fertilization	Chl *a*	Chl *b*	Chl *a*+*b*	Chl *a*	Chl *b*	Chl *a*+*b*	Chl *a*	Chl *b*	Chl *a*+*b*	Chl *a*	Chl *b*	Chl *a*+*b*
1. $N_{80}P_{35}K_{100}$	–	serie without Mg fertilization	140.8	51.2	192.0	23.5	24.2	47.7	66.9	28.2	95.1	77.1	34.5	111.6
2. N_{72} $P_{35}K_{100}$	N_8		140.9	51.9	192.8	26.1	24.3	50.4	70.6	28.9	99.5	79.2	35.0	114.2
3. N_{64} $P_{35}K_{100}$	N_{16}		141.4	51.5	192.9	30.5	24.6	55.1	71.8	29.4	101.2	81.2	35.2	116.4
4. N_{56} $P_{35}K_{100}$	N_{24}		144.6	52.2	196.8	35.3	27.5	62.8	76.9	31.6	108.5	85.6	37.1	122.7
5. N_{48} $P_{35}K_{100}$	N_{32}		145.0	55.6	200.6	38.9	28.2	67.1	78.4	30.4	108.8	87.4	38.1	125.5
6. N_{40} $P_{35}K_{100}$	N_{40}		146.3	55.4	201.7	51.7	32.9	84.6	78.1	29.7	107.8	92.0	39.3	131.3
		Mean:	143.2	53.0	196.1	34.3	27.0	61.3	73.8	29.7	103.5	83.8	36.5	120.3
7. $N_{80}P_{35}K_{100}$	–	24 kgMg · ha^{-1} applied before planting to the soil	139.1	55.5	194.6	55.9	28.8	84.7	83.5	29.4	112.9	92.8	37.9	130.7
8. N_{72} $P_{35}K_{100}$	N_8		138.4	56.3	194.7	56.5	28.4	84.9	85.5	29.5	115.0	93.5	38.1	131.6
9. N_{64} $P_{35}K_{100}$	N_{16}		141.9	56.7	198.6	57.3	29.8	87.1	87.7	32.6	120.3	95.6	39.7	135.3
10. N_{56} $P_{35}K_{100}$	N_{24}		143.0	57.0	200.0	60.1	29.1	89.2	88.4	34.6	123.0	97.2	40.2	137.4
11. N_{48} $P_{35}K_{100}$	N_{32}		141.1	58.1	199.2	59.2	29.1	88.3	88.6	33.1	121.7	96.3	40.1	136.4
12. N_{40} $P_{35}K_{100}$	N_{40}		142.0	58.8	200.8	60.4	29.9	90.3	87.1	32.1	119.2	96.5	40.3	136.8
		Mean:	140.9	57.1	198.0	58.2	29.2	87.4	86.8	31.9	118.7	95.3	39.4	134.7

Table 1 contd.

Treatments			2005			2006			2007			Mean 2005–2007		
NPK fertilization to the soil	foliar N fertilization	Mg fertilization	Chl *a*	Chl *b*	Chl *a*+*b*	Chl *a*	Chl *b*	Chl *a*+*b*	Chl *a*	Chl *b*	Chl *a*+*b*	Chl *a*	Chl *b*	Chl *a*+*b*
13. $N_{80}P_{35}K_{100}$	–	12 kgMg · ha^{-1} applied as foliar spraying	127.4	50.7	178.1	51.4	25.3	76.7	73.1	28.6	101.7	84.0	34.9	118.9
14. N_{72} $P_{35}K_{100}$	N_8		128.8	51.0	179.8	50.6	25.2	75.8	74.8	28.9	103.7	84.7	35.0	119.7
15. N_{64} $P_{35}K_{100}$	N_{16}		130.8	51.2	182.0	51.4	28.2	79.6	75.0	31.4	106.4	85.7	36.9	122.6
16. N_{56} $P_{35}K_{100}$	N_{24}		136.0	50.7	186.7	51.7	28.7	80.4	76.6	29.4	106.0	88.1	36.3	124.4
17. N_{48} $P_{35}K_{100}$	N_{32}		126.6	49.9	176.5	51.0	29.1	80.1	78.4	28.9	107.3	85.3	36.0	121.3
18. N_{40} $P_{35}K_{100}$	N_{40}		123.0	47.2	170.2	52.3	30.5	82.8	77.8	28.4	106.2	84.4	35.4	119.8
Mean:			128.8	50.1	178.9	51.4	27.8	79.2	76.0	29.3	105.2	85.4	35.8	121.1
Mean for three series:			137.6	53.4	191.0	48.0	28.0	76.0	78.8	30.3	109.1	88.1	37.2	125.4
LSD $_{(\alpha=0.05)}$ share of N applied to leaves in the total N dose			n.s.	n.s.	n.s.	4.30	1.29	5.42	3.83	1.54	4.17	n.s.	n.s.	n.s.
Magnesium fertilization technology			9.91	3.49	11.36	3.04	0.91	3.83	2.71	1.09	2.95	n.s.	n.s.	n.s.
Interaction			n.s.	n.s.	n.s.	7.46	2.24	9.40	6.63	2.68	7.22	n.s.	n.s.	n.s.

n.s. – non-significant differences.

yields Fig. 2. In 2006–2007, a considerable fall in yields produced by the tested potato cultivar was noted. In these years, the average yields were 22.43 and 15.75 Mg tubers $\cdot$ ha^{-1}. The contributing factor was the high total rainfall in August 2006 (173 mm) and July 2007 (165 mm), which exceeded the multiyear average for these months by 135 % and 143 %, respectively. Nonetheless, under such unfavourable conditions, it was found out that the volume of yields was significantly positively correlated with the content of chlorophyll in leaves, a relationship which did not occur in 2005, when the yields were very high (Table 2). In 2006, the correlation coefficient r – Chl a+b Yield was 0.82 in the series not fertilized with Mg; in the series with Mg introduced to soil, it was 0.91 and in the series with foliar application of Mg, it equalled 0.89. In 2007, significant correlation Chl a+b Yield was determined only in the series fertilized with magnesium added to soil $r = 0.78$ and sprayed on leaves $r = 0.79$.

In the series without magnesium nutrition, the content of chlorophyll in leaves had no effect on the volume of yields. In the light of the above results, it seems reasonable to conclude that magnesium is a key element in the synthesis of chlorophyll and accumulation of yield, especially in years when the weather conditions are unfavourable.

Significant influence of magnesium fertilization on the content of chlorophyll in leaves has also been reported by Ciecko et al [3], Grzebisz et al [5] and Seidler and Mamzer [15]. This element participates directly in the synthesis of chlorophyll, having direct impact on assimilation. Improved magnesium nutrition of plants enables them to incorporate some of otherwise potentially unused resources of soil nitrogen to biomass, which enhances the useful plant yield [5]. In this research, the sum (Chl a+b) in the series with the soil fertilization of magnesium in the dose of 24 kgMg $\cdot$ ha^{-1} was 134.7 and in the series where 12 kgMg $\cdot$ ha^{-1} of magnesium was sprayed on leaves, it equalled 121.1; in the series without magnesium fertilization, it was 120.3 mg $\cdot$ 100 g^{-1} fresh mass (Table 1). Soil magnesium fertilization contributed to increasing the content of individual forms of chlorophyll by 11.5 mg Chl a $\cdot$ 100 g^{-1} fresh mass, *ie* by 13.7 %, and by 2.8 mg Chl b $\cdot$ 100 g^{-1} fresh mass, *ie* 7.6 % compared with the content of chlorophyll found in tubers of potato plants fertilized with nitrogen alone. Magnesium produced the most profound impact on chlorophyll concentration in leaves in 2006. In that year, the increase in the sum of Chl a+b in potato leaves owing to soil magnesium fertilization was 26.1 mg $\cdot$ 100 g^{-1} fresh mass. Significant influence of magnesium fertilization was demonstrated in some earlier studies on the potato [3, 31]. However, the positive effect, *ie* increased concentration of chlorophyll in potato leaves, was achieved only when magnesium was applied to leaves. In the present study, soil application had a more beneficial influence, which may be indicative of differentiated action of this element, modified by agronomic and weather conditions.

Nitrogen foliar fertilization applied in amounts from 10 % to 50 % of the full dose of this nutrient contributed to a linear increase in the content of both forms of chlorophyll. In all the years, significant positive correlation was observed between the rising share of N applied to leaves in the total nitrogen dose and the content of chlorophyll (Table 2). Among the treatments without magnesium fertilization, the highest three-year average content of Chl a, Chl b and Chl a+b in potato leaves was found in leaves of potatoes growing on the plots where 40 kgN $\cdot$ ha^{-1}, *ie* 50 % of the full dose of nitrogen,

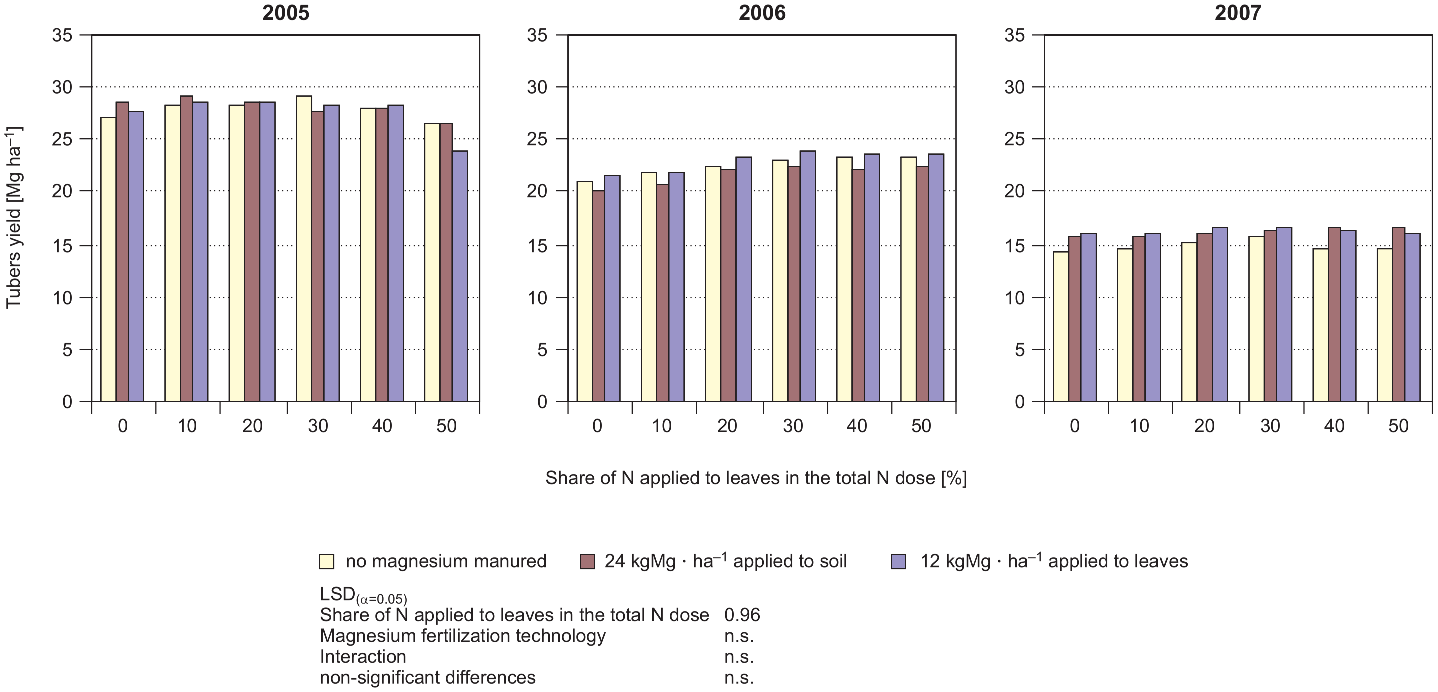

Fig. 2. Effect of foliar nitrogen and two magnesium fertilization technologies on the volume of potato tuber yields in 2005–2007

Table 2

Effects of foliar nitrogen fertilization and two magnesium fertilization technologies on the correlation coefficient between nitrogen fertilization, chlorophyll content in the leaves and potato tubers yield

Analysed variables	2005			2006			2007			Mean 2005–2007		
	Chl *a*	Chl *b*	Chl *a*+*b*	Chl *a*	Chl *b*	Chl *a*+*b*	Chl *a*	Chl *b*	Chl *a*+*b*	Chl *a*	Chl *b*	Chl *a*+*b*
Serie without Mg fertilization												
Increasing rate of foliar N in N dose × Yield	n.s.			0.95			n.s.			n.s.		
Increasing rate of foliar N in N dose × Chl content	0.95	0.88	0.95	0.96	0.92	0.95	0.96	0.64	0.92	0.99	0.97	0.99
Chl content × Yield	n.s.	n.s.	n.s.	0.84	0.76	0.82	n.s.	0.74	n.s.	n.s.	n.s.	n.s.
24 kgMg · ha^{-1} applied before planting to the soil												
Increasing rate of foliar N in N dose × Yield	–0.88			0.85			0.97			n.s.		
Increasing rate of foliar N in N dose × Chl content	0.70	0.99	0.91	0.93	0.64	0.94	0.76	0.68	0.74	0.86	0.91	0.88
Chl content × Yield	–0.73	–0.84	–0.86	0.86	0.75	0.91	0.82	0.72	0.78	0.70	0.70	0.70
12 kgMg · ha^{-1} applied as foliar spraying												
Increasing rate of foliar N in N dose × Yield	–0.59			–0.87			n.s.			n.s.		
Increasing rate of foliar N in N dose × Chl content	n.s.	–0.76	n.s.	0.55	0.95	0.92	0.95	n.s.	0.84	n.s.	n.s.	n.s.
Chl content × Yield	0.63	0.95	0.76	0.51	0.93	0.89	n.s.	0.75	0.72	0.72	0.76	0.80

n.s. – non-significant correlation.

was applied as foliar spraying (Table 1). The increment in chlorophyll induced by this fertilization variant, compared with the treatments where all nitrogen was introduced to soil, was 14.9 mg Chl, mg Chl *a* · 100 g^{-1} fresh mass, *ie* 19.3 %, 4.8 mg Chl *b* · 100 g^{-1} fresh mass, *ie* 14 % and 19.7 mg Chl *a*+*b* · 100 g^{-1} fresh mass, *ie* 17.6 %. This increase was most noticeable in 2006, in which the rise in the content of Chl *a*+*b* caused by foliar application of nitrogen was 36.9 mg · 100 g^{-1} fresh mass. In the other years, foliar nitrogen fertilization did not exert such strong influence on the leaf content of chlorophyll. Likewise, in the both series amended with magnesium, foliar nitrogen fertilization had a positive effect on the content of chlorophyll. The highest concentration of chlorophyll was found in the treatments fertilized with 24 kgN · ha^{-1}, which corresponded to 30 % of the full nitrogen dose. This fertilization variant, compared with the one where all nitrogen dose was applied to soil, induced an average increase in the content of Chl *a*+*b* of 6.7 mg · 100 g^{-1} fresh mass, *ie* 5 % in the treatments with soil magnesium fertilization and 5.5 mg · 100 g^{-1}, *ie* 4.6 % in the treatments with foliar magnesium application. Stronger impact of foliar than soil magnesium application on synthesis of chlorophyll pigments demonstrated in the present experiment find confirmation in literature [3, 16].

Conclusions

1. Under the influence of an increasing share of N applied to leaves in the total nitrogen rate of 80 kgN · ha^{-1}, within the range of 8 to 40 kgN · ha^{-1}, a linear increase in the content of Chl *a* and Chl *b* in potato leaves appeared. The maximum increase in the content of these pigments was 16.2 and 12.2 %, respectively.
2. The applied magnesium nutrition had a positive effect on the content of both forms of chlorophyll. The rate of 24 kgMg · ha^{-1} had a more beneficial effect (134.7 mg Chl *a*+*b* · 100 g^{-1} fresh mass) than the rate of 12 kgMg · ha^{-1} sprayed over leaves (121.1 mg Chl *a*+*b* · 100 g^{-1} fresh mass).
3. In 2006 and 2007, which were unfavourable to potato yields, concentrations of chlorophyll in leaves were positively correlated with the yields. The correlation coefficients were within the range of $r = 0.78$ to $r = 0.91$, which may indicate a particularly important role of magnesium as an element directly affecting potato yields under the conditions that are not beneficial to potato cultivation.

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ODDZIAŁYWANIE DOLISTNEGO NAWOŻENIA AZOTEM I MAGNEZEM NA ZAWARTOŚĆ CHLOROFILU W LIŚCIACH ZIEMNIAKA

Katedra Chemii Środowiska
Uniwersytet Warmińsko-Mazurski w Olsztynie

Abstrakt: Celem badań było wyjaśnienie wpływu dolistnego nawożenia azotem i magnezem na kształtowanie się zawartości chlorofilu w liściach ziemniaka jadalnego średnio wczesnej odmiany Zebra. Zróżnicowane nawożenie dolistne azotem zastosowano w zakresie od 0 do 50 % pełnej dawki tego składnika (80 kgN · ha^{-1}). Eksperyment przeprowadzono w trzech seriach – bez nawożenia magnezem, z magnezem stosowanym doglebowo (24 kgMg · ha^{-1}) oraz z magnezem stosowanym dolistnie (12 kgMg · ha^{-1}). Największą zawartość chlorofilu *a* i *b* uzyskano w 2005 r. – 137,6 mg i 53,4 mg na 100 g świeżej masy liści. W roku tym uzyskano jednocześnie najwyższy plon bulw – średnio 27,86 Mg · ha^{-1}. W latach następnych nie potwierdzono tej zależności. Wzrastający udział N stosowanego dolistnie w ogólnej dawce azotu spowodował praktycznie liniowy przyrost ilości obu form chlorofilu. W latach niesprzyjających plonowaniu 2006 i 2007 stwierdzono, że ilość plonów była dodatnio skorelowana z zawartością chlorofilu w liściach, czego nie stwierdzono w roku 2005, w którym plon był największy. Zastosowany doglebowo, jak i dolistnie magnez miał decydujące znaczenie w syntezie chlorofilu i nagromadzaniu plonu szczególnie w latach o niesprzyjających warunkach pogodowych.

Słowa kluczowe: chlorofil, nawozy mineralne, magnez, azot, plon bulw, *Solanum tuberosum*, ziemniak

Monika TABAK[1] and Barbara FILIPEK-MAZUR[1]

CONTENT AND UPTAKE OF NITROGEN BY MAIZE FERTILIZED WITH ORGANIC MATERIALS DERIVED FROM WASTE

ZAWARTOŚĆ I POBRANIE AZOTU PRZEZ KUKURYDZĘ NAWOŻONĄ MATERIAŁAMI ORGANICZNYMI POCHODZENIA ODPADOWEGO

Abstract: The aim of the research was to determine influence of organic materials fertilization on amount of maize yield as well as on nitrogen content in plants and on amount of uptaken nitrogen. The three-year field experiment comprised 7 treatments: non-fertilized soil (control) and soil fertilized with mineral fertilizers: manure, compost from green waste, sewage sludge, compost from sewage sludge and wheat straw as well as with a mixture of sewage sludge and hard coal ash. Maize harvested for silage was the test plant. Nitrogen content in the maize top parts was assessed by Kjeldahl method.

The yield-forming effect of the compost from green waste and of the sewage sludge was more favorable than the effect of the compost from sludge and straw and the mixture of sludge and ash, and similar to the effect of the manure and the mineral fertilizers. The weighted mean nitrogen content in the fertilized maize was higher than in the control plants. The highest mean element content was assessed in the maize fertilized with the compost from sludge and straw and with the mixture of sludge and ash (as a result of nitrogen cumulation in a relatively small yield of the plants fertilized with those materials). In the 1st year of the research, the amount of nitrogen uptaken from the soil fertilized with the mineral fertilizers was the highest, while in the following years the amount of nitrogen uptaken from the soil fertilized with the manure and organic materials was higher. The total amount of nitrogen uptaken from the soil fertilized with the mineral fertilizers, the manure, the compost from green waste and the sewage sludge was the highest.

Keywords: nitrogen, organic materials, waste, compost, sewage sludge, maize

In order to properly supply plants with nutrients, in conditions of fertilization with organic material, it is not sufficient to introduce an adequate dose of elements, which is established on the basis of their total content in the material. Degree of availability of elements from soil, after fertilization, should also be taken into consideration. It will allow not only to satisfy nutrient requirements of plants but also to limit risk of

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[1] Department of Agricultural and Environmental Chemistry, University of Agriculture in Krakow, al. A. Mickiewicza 21, 31–120 Kraków, Poland, phone: +48 12 662 43 47, fax: +48 12 662 43 41, email: Monika.Tabak@ur.krakow.pl

environmental pollution caused by leaching and volatilization of nutrients. Organic materials, depending on their origin, differ in content of element forms directly available for plants and in rate of converting from bound forms of nutrients to available forms [1].

The aim of the research was to determine influence of fertilization with organic materials derived from waste on amount of maize yield as well as on content of nitrogen in the maize and on amount of uptaken nitrogen. Moreover, the aim of the research was to establish value of coefficient of nitrogen utilization from organic materials.

Material and methods

The 3-year field experiment was set up in 2008 at an experimental station of the University of Agriculture in Krakow. The experiment was conducted on Eutric Cambisol, with grain-size distribution of light clay. The soil was characterized with acid reaction (pH_{KCl} = 5.40) and very high contents of available forms of phosphorus and potassium (respectively 94.9 mg and 219.2 mg $\cdot$ kg^{-1} d.m.). Content of organic carbon amounted to 9.88 g $\cdot$ kg^{-1} d.m. and content of total nitrogen amounted to 1.07 g $\cdot$ kg^{-1} d.m. The soil properties were suitable for agricultural use of sewage sludges [2]. Detailed information regarding the soil properties before establishing the field experiment can be found in the paper of Tabak and Filipek-Mazur [3].

The experiment comprised 7 treatments: a non-fertilized soil (control treatment) and a soil fertilized with mineral fertilizers, cattle manure, compost from green waste, sewage sludge, compost from sewage sludge and straw as well as with a mixture of sewage sludge and hard coal ash. Each treatment was carried out in 4 replications. The manure contained 28.49 gN, the compost from green waste contained 14.44 gN, the sewage sludge contained 20.19 gN, the compost from sludge and straw contained 24.48 gN and the mixture of sludge and ash contained 14.49 gN $\cdot$ kg^{-1} d.m. Content of trace elements in the organic materials used for fertilization did not exceeded the limit values established for agricultural use of sewage sludges [2]. Origin and properties of the organic materials used for fertilization were described in the paper of Tabak and Filipek-Mazur [3].

The doses of nutrient elements introduced in particular years to the soil of the fertilized treatments are shown in Table 1.

Table 1

Doses of the nutrient elements introduced to the soil in particular years [kg $\cdot$ ha^{-1}]

Year	N	P_2O_5	K_2O
1st year	160	168	140
2nd year	100	30	110
3rd year	100	30	110

In the 1st year of the research, to the soil fertilized with the manure and the organic materials, the whole nitrogen dose was introduced with the fertilizer and those materials. Ammonium nitrate, enriched superphosphate and potassium chloride were used to introduce the nutrient elements to the soil of the mineral treatment and also to even up the doses of phosphorus and potassium in the soil of the remaining fertilized treatments. The mentioned mineral fertilizers were also used to conduct fertilization in the 2nd and 3rd year of the field experiment.

The PR 39F58 maize (Pioneer) was the test plant in all years of the research and it was grown for silage. The mean temperature for the maize growing season was similar in all years and amounted to (16.2–16.3) °C (Table 2). That temperature was higher than the mean temperature sufficient for proper growth of maize, which amounts to about 15 °C [4]. However, in all years May and September were the cold months. In every year the sum of rainfall during the maize growing season exceeded the level of 300 mm (regarded as sufficient, with right distribution, for proper maize development [4]). However, the distribution and the amount of rainfall were not favorable. A water deficit occurred in May and June in the 1st year of the research, that deficit was replenished in July. In the 2nd year, in May and June an excess of rainfall occurred, whereas in the 3rd year of the experiment an excess of rainfall occurred during all months of maize growth.

Table 2

Mean monthly temperatures and monthly sums of rainfall

Parameter	Year	Month					
		V	VI	VII	VIII	IX	V–IX
Mean temperature [°C]	1st year	13.6	18.4	18.7	18.2	12.6	16.3
	2nd year	13.6	16.0	19.9	18.6	12.9	16.2
	3rd year	12.8	17.6	20.5	18.5	12.3	16.3
Sum of rainfall [mm]	1st year	28.7	26.7	142.6	41.6	98.8	338.4
	2nd year	106.6	122.1	82.7	53.3	61.5	426.2
	3rd year	299.0	135.2	105.2	127.5	112.8	779.7

The maize was harvested at wax maturity stage of the grain (proper for harvesting for silage). After the harvest the amount of fresh matter yield of the maize top parts was determined. Then, after desiccating at 70 °C in a dryer with hot air flow, the content of dry matter in the maize top parts was determined. The amount of dry matter yield of the maize top parts harvested from a given object was calculated basing on the mean amount of the fresh matter yield obtained from that treatment and the mean content of dry matter in that yield.

The content of total nitrogen in dry and melted plant material was determined with Kjeldahl method [5], after reduction of nitric form to ammonium form. The assessment was conducted on Kjeltec 2300 (FOSS) apparatus. The mean nitrogen content in biomass was counted as a weighted mean.

The results were formulated statistically using Statistica 8.0 program. A univariate analysis of variation was carried out, and the significance of differences between the mean values was estimated using the Duncan test (α = 0.05).

Results and discussion

The used fertilization led to an increase of the total (from 3 years) yield of the maize (Table 3). The total fresh matter yield of the top parts of the maize fertilized with the organic materials was higher by 25.9–37.2 % than the control yield, and the total dry matter yield was higher by 31.5–51.9 %. The described beneficial yield-forming effect of the organic materials derived from waste is consistent with literature data [6–10]. However, some authors indicate a possibility of decreasing plant yield as a result of fertilization with organic materials [11].

Table 3

Total (from 3 years) yield of maize [Mg $\cdot$ ha^{-1}]

Treatment	Total fresh matter yield of maize top parts	Total dry matter yield of maize top parts
No fertilization	140.91 a*	45.88
Mineral fertilizers	205.10 d	68.10
Manure	195.04 cd	68.96
Compost from green waste	191.79 c	69.69
Sewage sludge	193.29 c	67.17
Compost from sewage sludge and straw	178.32 b	60.32
Mixture of sewage sludge and ash	177.42 b	62.16

* Mean values in columns marked with the same letters do not differ statistically significantly at $\alpha = 0.05$, according to the Duncan test.

The compost from green waste and the sewage sludge were characterized with yield-forming effect similar to the manure, and – while analyzing the dry matter yield – also to the mineral fertilizers (Table 3). From among the examined fertilization types, the compost from sewage sludge and straw as well as the mixture of sewage sludge and ash had the weakest yield-forming effect. Contrary to the Authors' own research, Krzywy and Woloszyk [10] stated that yield-forming effect of sewage sludge and composts from sewage (with addition of straw, sawdust or leaves) was similar to effect of mineral fertilizers or better than that. Moreover, the yield-forming effect of using the composts was more favorable than the effect of using only the sludge or similar to it. Gondek et al [9] also established that yield of plants fertilized with sewage sludges as well as with mixtures of sewages and peat was usually higher than yield of plants fertilized with mineral salts. Adding peat to the sludge had a beneficial influence on the yield-forming effect of the organic material. However, Gondek and Filipek-Mazur [8] showed a weaker effect of organic material (compost from plant residues) than of mineral salts. In the cited research [8, 9] it was found that the organic materials were characterized with the yield-forming effect similar to manure or better than it. Those results were not always confirmed in the Authors' own research. Doses of nitrogen, phosphorus and potassium were balanced in fertilized treatments both in the Authors' own research and in the researches of Gondek and Filipek-Mazur [8], Gondek et al [9] as well as of Krzywy and Woloszyk [10]. Therefore, differences in the influence of

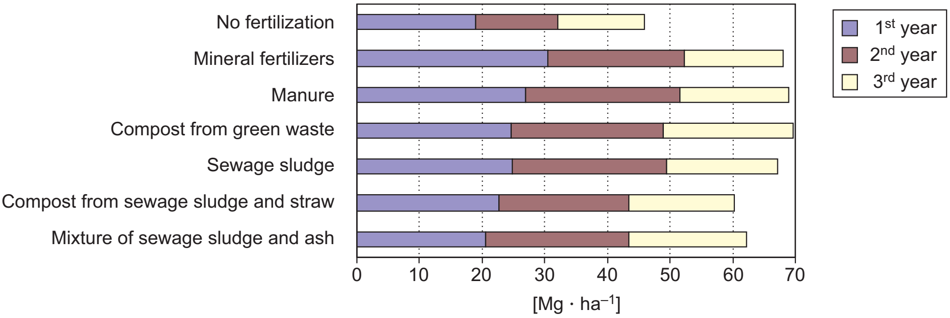

Fig. 1. Dry matter yield of maize top parts

particular types of fertilization on the amount of plants yield should not be explained by different doses of those elements, but rather by differentiated content of available forms in soil of particular treatments. More favorable effect of mineral fertilization in the 1st year of the investigations, stated in the Authors' own research (Fig. 1) and also by Gondek et al [9], can be explained by higher availability of the elements from the soil fertilized minerally than from the soil fertilized with organic matter. In the following years the difference between effects of mineral fertilizers and of organic materials diminished, in consequence of releasing elements from organic matter. Beneficial yield-forming effect of organic materials is also a result of introducing some nutrients present in those materials (elements other than nitrogen, phosphorus and potassium) to soil. Also Gondek et al [9] point that out.

In the 1st year of the field experiment, a statistically significant influence of the fertilization on the nitrogen content in the maize top parts was not stated, in comparison with the content determined in the non-fertilized maize (Table 4).

Table 4

Nitrogen content in the maize top parts [g · kg^{-1} d.m.]

Treatment	1st year	2nd year	3rd year	Mean content
No fertilization	11.64 ab*	8.18 a	10.82 ab	10.40
Mineral fertilizers	11.95 b	8.58 ab	11.32 b	10.73
Manure	11.14 a	9.96 c	10.54 a	10.57
Compost from green waste	11.04 a	9.17 b	12.47 c	10.81
Sewage sludge	11.70 ab	10.23 c	10.50 a	10.85
Compost from sewage sludge and straw	12.13 b	10.51 c	11.10 ab	11.28
Mixture of sewage sludge and ash	12.12 b	10.33 c	11.00 ab	11.12

* See Table 3.

However, Wieczorek and Gambus [11] indicate a possibility of increasing nitrogen content in plants already in the year of applying sludges. In the Authors' own research, the greatest influence of the fertilization on the nitrogen content in the test plants was noticed in the 2nd year of the research – statistically significantly higher nitrogen content was obtained in the maize fertilized with the manure and the organic materials than in the non-fertilized plants. The maize fertilized with the manure, the sewage sludge and the materials containing sludge contained 21.8–28.5% more nitrogen than the plants gathered from the control object; the maize fertilized with the compost from green waste contained 12.1 % more nitrogen. In the 3rd year of the research only the fertilization with the compost from green waste statistically significantly influenced the nitrogen content in the plants, in comparison with the content in the control maize (the content higher by 15.3 %). The weighted mean nitrogen content in the maize top parts was higher in the fertilized treatments (between 10.6 $\mathrm{g \cdot kg^{-1}}$ d.m. and 11.3 $\mathrm{g \cdot kg^{-1}}$ d.m.) than in the control (10.4 $\mathrm{g \cdot kg^{-1}}$ d.m.) (Table 4). The highest mean nitrogen content was assessed in the maize fertilized with the compost from sewage sludge and straw as well as with the mixture of sewage sludge and ash. It was a result of nitrogen cumulation in a relatively small yield gathered from the treatments fertilized with those two materials (Table 3, Fig. 1). Gondek et al [9] also stated that fertilization with organic materials led to an increase in nitrogen content in maize top parts. However, the authors obtained higher nitrogen content in plants fertilized with mineral salts than with manure and organic materials.

The content of total protein in the plants fertilized with the organic materials was in the range (57.31; 77.96) $\mathrm{g \cdot kg^{-1}}$ d.m. (the protein content was obtained by multiplying the total nitrogen content by 6.25). That content was lower than the proper value given in literature for maize for silage, which is about 80–90 $\mathrm{g \cdot kg^{-1}}$ d.m. [4, 12]. The content of total protein in the non-fertilized maize as well as in the maize fertilized with the mineral fertilizers and with the manure also did not exceed 80 $\mathrm{g \cdot kg^{-1}}$ d.m.

In the 1st year of the research, the highest maize yield was gathered from the object fertilized with the mineral fertilizers (Fig. 1). What is more, those plants were characterized with a relatively high nitrogen content (Table 4). As a result, in the 1st year of the research the amount of nitrogen uptaken from the soil fertilized with the mineral fertilizers was the highest (Table 5).

Table 5

Amount of nitrogen uptaken by maize [$\mathrm{kg \cdot ha^{-1}}$]

Treatment	1st year	2nd year	3rd year	Total uptake
No fertilization	220.3	107.4	149.4	477.2
Mineral fertilizers	365.0	186.2	179.4	730.6
Manure	300.7	245.7	182.3	728.7
Compost from green waste	271.9	222.6	259.1	753.7
Sewage sludge	291.1	251.0	186.4	728.5
Compost from sewage sludge and straw	276.2	216.9	187.5	680.6
Mixture of sewage sludge and ash	249.3	236.6	205.4	691.4

That indicates higher availability, in the 1st year of research, of nitrogen from that soil than from the soil fertilized with the manure and the organic materials. In the 2nd and 3rd years, the amount of nitrogen uptaken from the soil fertilized with the manure and with the organic materials was higher than the amount of nitrogen uptaken from the soil fertilized with mineral fertilizers. That indicates mobilization of nitrogen introduced to the soil in organic form. The total amount of uptaken nitrogen was the highest from the soil fertilized with the mineral fertilizers, the manure, the compost from green waste and the sewage sludge (it amounted to 152.7–157.9 % of the amount of nitrogen uptaken from the control soil).

Maize belongs to plants that well utilize nutrients from fertilizers containing organic matter [13]. In 1st year after manure application nitrogen utilization by maize amounts to about 25–40 %, whereas in the 2nd and 3rd – to about 35–40 % [13]. However, values obtained in researches concerning utilization of nitrogen from organic materials derived from waste were lower than the ones given above. Mackowiak argues that immediate nitrogen utilization from sewage sludges usually amounts to about 20 % and sequential utilization amounts to about 10 % [14]. Mazur et al [15] stated that nitrogen utilization in the year of applying composts from sewage sludge with different additives (sawdust, brown coal, slops) amounted to 12–19 %. With additional mineral nitrogen fertilization the utilization amounted to (33; 38) %. Czyzyk et al [7] obtained higher nitrogen utilization from composts from sewage sludge and straw when organic material was characterized with higher content of nitrate and ammonium nitrogen (therefore available forms). In the Authors' own research, the value of the coefficient of nitrogen utilization from the mineral fertilizers and the manure was the same and amounted to 70 %. The utilization of nitrogen from the compost from green waste was higher (77 %), from the sewage sludge it was the same (70 %), whereas from the materials prepared basing on the sludge it was lower (57; 59) % than the utilization from the mineral fertilizers and the manure. The level of nitrogen utilization from the organic materials was relatively high – it most probably resulted from the fact that the fertilization with the organic materials was combined with the mineral nitrogen fertilization.

Conclusions

1. Fertilization with organic materials derived from waste beneficially influenced the amount of the maize yield. Both the compost from green waste and the sewage sludge had more favorable yield-forming effect than the compost from sewage sludge and straw and the mixture of sewage sludge and ash. Moreover, the effect of the compost from green waste and of the sludge approximated the effect of the manure and the mineral fertilizers.

2. The greatest influence of the fertilization on the nitrogen content in the test plants was noticed in the 2nd year of the research. At that time, fertilization with the manure and the organic materials led to an increase of the nitrogen content in plants, in comparison with the control. Weighted mean nitrogen content in the maize top parts was higher in the fertilized treatments (between 10.57 g $\cdot$ kg^{-1} d.m. and 11.28 g $\cdot$ kg^{-1} d.m.) than in the control (10.40 g $\cdot$ kg^{-1} d.m.). The highest mean nitrogen content was found in the maize fertilized with the compost from sewage sludge and straw as well as with the mixture of sewage sludge and ash.

3. In the 1st year of the field experiment, the amount of nitrogen uptaken by the plants fertilized with the mineral fertilizers was the highest. In the following years, as a result of mineralization of organic nitrogen compounds, the amount of nitrogen uptaken from the soil fertilized with the manure and the organic materials was higher than the amount of nitrogen uptaken from the soil fertilized with the mineral fertilizers. Totally during 3 years, the amount of nitrogen uptaken by the plants fertilized with the mineral fertilizers, the manure, the sewage sludge and the compost from green waste was the highest (152.7; 157.9) % of the amount of nitrogen uptaken from the control soil).

4. The utilization of nitrogen from the compost from green waste and the sewage sludge was higher than the utilization of that element from the compost from sludge and straw and the mixture of sewage sludge and ash.

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ZAWARTOŚĆ I POBRANIE AZOTU PRZEZ KUKURYDZĘ NAWOŻONĄ MATERIAŁAMI ORGANICZNYMI POCHODZENIA ODPADOWEGO

Katedra Chemii Rolnej i Środowiskowej
Uniwersytet Rolniczy im. Hugona Kołłątaja w Krakowie

Abstrakt: Celem badań było określenie wpływu nawożenia materiałami organicznymi na wielkość plonu kukurydzy, zawartość azotu w roślinach oraz ilość pobranego azotu. Przeprowadzono trzyletnie doświadczenie polowe obejmujące 7 obiektów: glebę nienawożoną (kontrola) oraz glebę nawożoną nawozami mineralnymi, obornikiem, kompostem z odpadów zielonych, osadem ściekowym, kompostem z osadu ściekowego i słomy pszennej oraz mieszaniną osadu ściekowego i popiołu z węgla kamiennego. Rośliną testową była kukurydza uprawiana na kiszonkę. Zawartość azotu ogólnego w roślinach oznaczono metodą destylacyjną Kjeldahla.

Plonotwórcze działanie kompostu z odpadów zielonych i osadu ściekowego było korzystniejsze niż działanie kompostu z osadu i słomy oraz mieszaniny osadu i popiołu, a jednocześnie zbliżone do działania obornika i nawozów mineralnych. Średnia ważona zawartość azotu w częściach nadziemnych kukurydzy nawożonej była większa niż w roślinach kontrolnych. Największą średnią zawartość pierwiastka stwierdzono w kukurydzy nawożonej kompostem z osadu i słomy oraz mieszaniną osadu i popiołu (na skutek kumulacji azotu w stosunkowo małym plonie roślin nawożonych tymi materiałami). W pierwszym roku badań największa była ilość azotu pobranego z gleby nawożonej nawozami mineralnymi, natomiast w kolejnych latach większa była ilość azotu pobranego z gleby nawożonej obornikiem i materiałami organicznymi. Analizując dane sumaryczne stwierdzono, że największa była ilość azotu pobranego z gleby obiektów nawożonych nawozami mineralnymi, obornikiem, kompostem z odpadów zielonych i osadem ściekowym.

Słowa kluczowe: azot, materiały organiczne, odpady, kompost, osad ściekowy, kukurydza

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Katarzyna BOROWSKA[1], Jan KOPER[1]
and Marlena GRABOWSKA[1]

IMPACT OF FARMYARD MANURE AND DIFFERENT DOSES OF NITROGEN ON THE AVAILABILITY OF SELENIUM BY SPRING BARLEY (*Hordeum vulgare* L.)

WPŁYW NAWOŻENIA OBORNIKIEM I ZRÓŻNICOWANYMI DAWKAMI AZOTU NA PRZYSWAJALNOŚĆ SELENU PRZEZ JĘCZMIEŃ JARY (*Hordeum vulgare* L.)

Abstract: The objective of the study was to determine the total selenium content and its fractions available to spring barley plants affected by FYM and different doses of nitrogen. Comparison of the results of total soil Se concentration reported in this paper with other findings indicated that analysed soil had a very low selenium content. Such low levels of selenium in soils indicated that plants growing on these soils are deficient in this microelement. The application of manure and nitrogen resulted in the highest amounts of total selenium content in soil, which increased with increasing doses of both fertilizers. Fertilization with manure resulted in an increase of selenate and selenite in soil with increasing doses of manure, but the nitrogen treatment did not effect on the content of this fractions of selenium in soil. The share of Se-phytoavailable fractions in the total selenium content in soil under study ranged from 13.5 to 27.3 % and increased with increasing doses of FYM. Generally, the selenium concentrations in aboveground parts and roots of spring barley increased with increasing doses of FYM, but the application of nitrogen decreased the Se content in the investigated parts of plants.

Keywords: selenium, spring barley, farmyard manure, nitrogen fertilization

Selenium plays an important role in biological systems and the concentration range in which selenium is essential is narrow. As a natural constituent of soil minerals, selenium is normally present in soil at low contents ranging from 0.01 to 2 mg · kg^{-1}, but in most agricultural areas, soils contain so little available selenium that cultivated crops usually do not absorb more than traces of this element [1, 2]. The concentration and chemical forms of selenium in soils are governed by various chemical and physical

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[1] Department of Biochemistry, University of Technology and Life Sciences, ul. Bernardyńska 6, 85–029 Bydgoszcz, Poland, phone: +48 52 374 95 56, fax: +48 52 374-95-05, email kborowska56@o2.pl

factors, including pH, chemical and mineralogical composition, adsorbing surface, and oxidation and reduction status [2]. In Poland the dietary Se intake is on average 11–24 $\mu g \cdot d^{-1}$, what is about 4-times lower than the recommended level of 75 $\mu g \cdot d^{-1}$ for man and 60 $\mu g \cdot d^{-1}$ for woman set by World Health Organization (WHO) [3]. To minimize the occurrence of health problems, such as cancer and cardiovascular and viral diseases, which can be induced by selenium deficiency, increasing the selenium concentration in foods is an good way of Se supply to humans [4]. Cereals as the major foodstuff may offer the best opportunity to do so. According to Stadlober [5] and Seppanen et al [6], selenium levels in crops can be secured by agronomic biofortification *eg* either by adding organic supplements of high level selenium (sewage sludge, manure of selenium-supplemented farm animals or by adding selenate containing mineral fertilizers. The inorganic selenium compounds applied in fertilizers are taken up by plants and assimilated into valuable organic Se-compounds, which are safer and their retention in tissue is better. This paper presents the results of field investigations on total selenium and its phytoavailable fractions concentrations in soil long-term fertilized with farmyard manure and nitrogen. The availability of selenium by spring barley is also reported.

Materials and methods

Soil and plant samples were collected from the long-term static experiment established at the Agricultural Experimental Station at Grabow carried out since 1980 by the Department of Plant Nutrition of the Institute of Soil Science and Cultivation in Pulawy. The experiment was conducted applying the following crop rotation system: potato – winter wheat + intercrop – spring barley + undersown and red clover + grasses, designed in a split-plot with four replications (sub-plots). Organic fertilizer in a form of cattle manure (FYM) was applied under potato in the doses of 0, 20, 40, 60 and 80 $Mg \cdot ha^{-1}$ (factor A) and nitrogen at the doses of 0, 40, 80 and 120 $kgN \cdot ha^{-1}$ was used under spring barley (factor B). Soil and plant samples were collected in the 23rd year of the experiment, in May 2003, from the 0–20 cm layer under spring barley. Soil samples were air-dried and sieved through a 2 mm screen. Spring barley was rinsed in deionised water to remove soil particles, separated into aboveground biomass and roots, and dried. The total selenium content was determined by the method of Watkinson [7] using a Hitachi F-2000 spectrofluorometer. Soil samples were microwave digested with concentrated nitric(V) and perchloric(VII) acids. The different forms of selenium in the samples were reduced by boiling with 10 % HCl. The selenium was complexed with 2,3-*diaminonaphtalene* (DAN) to the fluorescent compound, which was extracted with cyclohexane and read on the spectrofluorometer at excitation and emission wavelengths of λ = 376 nm and 519 nm, respectively. The analytical procedures provided satisfactory values for the standard reference material CRM024-050 from the *Resource Technology Corporation* (RTC); determined value was 0.558 $mgSe \cdot kg^{-1}$ (certified value – 0.540 $mg \cdot kg^{-1}$). The certified reference material was included in each batch of samples for quality control. Available to plants forms of selenium were extracted from the soil by the part of sequential extraction method recommended by Chao and Sanzolone [8] with modification of Wang and Chen [2]. Firstly, 0.25 M KCl solution was used to extract the soluble form of selenium (Se(VI)). The exchangeable and specifically adsorptive forms of selenium (Se(IV)) were extracted by 0.1 M KH_2PO_4 solution. The final reaction solution of each extraction was adjusted with dilute HCl to a pH range 1.7–2.0. The selenite (Se^{4+}) was then cheleated by adding 2,3-diamino-naphtalene to the solution and determined by fluorescence spectrophotometry. The soil samples were analysed for granulometric composition according to Bouyoucos-Casagrande method, organic carbon by wet oxidation with potassium dichromate, total nitrogen following by Kjeldahl method and pH in distilled water and 1 M KCl potentiometrically.

Two-way analysis of variance (ANOVA) was used to identify significant differences ($p < 0.05$) between Se concentrations in parts of plants, corresponding soil and speciation. Data analysis was carried out using Statistica 8.0 for Windows Stat. Soft. Inc.

Results and discussion

The general properties of the soil under study are given in Table 1. The soil, according to the FAO classification, was classified as Haplic Luvisols and demonstrated

Table 1

General properties of soil under study

Sample symbol	Soil particle size fraction [%]		pH		C_{org} [$g \cdot kg^{-1}$]	N_{tot} [$g \cdot kg^{-1}$]
	< 0.02 [mm]	< 0.002 [mm]	H_2O	KCl		
0-N0	18	6	6.1	5.5	7.55	0.679
0-N1	17	6	6.3	5.5	7.60	0.683
0-N2	19	8	6.3	5.4	7.14	0.711
0-N3	17	7	6.1	5.2	7.29	0.728
20-N0	14	5	6.2	5.5	8.10	0.707
20-N1	16	8	6.1	5.4	7.89	0.721
20-N2	15	6	6.1	5.4	8.05	0.739
20-N3	18	7	6.1	5.4	7.73	0.760
40-N0	19	8	6.2	5.5	8.37	0.749
40-N1	17	6	6.2	5.4	7.61	0.728
40-N2	13	5	6.2	5.4	9.24	0.812
40-N3	19	6	6.2	5.2	9.48	0.851
60-N0	16	5	6.2	5.5	9.67	0.854
60-N1	16	6	6.2	5.4	9.87	0.826
60-N2	19	7	6.2	5.6	10.05	0.861
60-N3	20	6	6.2	5.5	9.96	0.865
80-N0	15	4	6.2	5.5	9.35	0.917
80-N1	16	6	6.3	5.6	9.94	0.931
80-N2	15	5	6.3	5.4	9.78	0.959
80-N3	14	5	6.2	5.1	10.23	0.949

the texture of loamy sand and sandy loam. The pH values of soil were in the slightly acidic range under which conditions Se exist predominantly as selenite in well-drained soils [4]. The application of manure resulted in the highest contents of organic carbon and total nitrogen in soil, especially treated with FYM at the doses of 60 and 80 Mg · ha^{-1}. The total soil Se concentration varied from 0.108 (control plots) to 0.170 mg · kg^{-1} from plots with the highest doses of farmyard manure (Table 2). Such low levels of selenium in soils indicated that plants growing on these soils are deficient in this microelement. According to Kabata-Pendias [1], the mean total selenium content in the soils worldwide is estimated as 0.44 mg · kg^{-1}, while its background contents in various soil groups range 0.05–1.5 mg · kg^{-1} being the lowest in Podzols and the highest in Histosols. Total selenium content in soil under study was affected by organic and nitrogen fertilization. The application of manure resulted in the highest amounts of total selenium content in soil (Table 2), which increased with increasing doses of manure and nitrogen. The Se content in soil from plots fertilized with FYM at the dose of 80 kg · ha^{-1} rose in average above 30 % in comparison with control. Sager [9] and Broadley et al [10] reported that selenium is present in various manures in amounts varying from 0.32 to 2.4 mg · kg^{-1}. Thus, the increase in Se in FYM-treated soil could have been due to the amount of this microelement in FYM.

On account of the existence of different Se species in soils, total selenium concentrations does not necessarily reflect the extent to which growing plants take up selenium [5]. Additionally knowledge of different species of Se, particularly phyto-available, present in soil is required to understand the biological and environmental impact of this element. In the present study the concentration of soluble and exchangeable forms of selenium, which are presumably plant available, were in the range 0.015–0.048 mg · kg^{-1} (Table 2). Fertilization with manure resulted in an increase of selenate and selenite in soil with increasing doses of manure. However, following the nitrogen treatment did not effect on the content of this fractions of selenium in soil. The share of Se-phytoavailable fractions in the total selenium content in soil under study ranged from 13.5 to 27.3 % and increased with increasing doses of FYM. In soil under study we found the higher share of selenite(IV) than selenate(VI) in the total selenium content. Selenate, which is poorly adsorbed on oxide surfaces and thus the most mobile Se form, can be expected to occur under high oxidative conditions. At low redox potential it can be reduced to selenite, which has a much higher adsorption affinity. It is strongly retained by ligand exchange on oxide surfaces, especially at low pH, which reduces its bioavailability [1, 11]. The transformation of easily soluble selenates added to acidic or neutral soils into slightly soluble forms is relatively fast [1]. Wang and Chen [2] pointed out that organic matter in soil affects bioavailability of selenium in soil; the content of soil Se is strongly influenced by leaching and hydrological transport processes; low selenium in soils have developed on the low selenium parent material with a very low flux of selenium between soil and plants.

In the present study the average selenium content in upper parts of spring barley from control plots reached 0.130 mg · kg^{-1} d.m. (Table 2). Generally, the selenium concentrations in aboveground parts and roots of spring barley increased with increasing doses of FYM. In upper parts of spring barley treated with the dose of 80 Mg · ha^{-1}, the

Table 2

Total and phytoavailable selenium content in soil and spring barley [mg · kg^{-1}]

Sample symbol	Se$_{tot}$ in soil	Se(VI) in soil	Se(IV) in soil	Se in spring barley	
				aboveground parts	roots
0-N0	0.119	0.016	0.021	0.136	0.154
0-N1	0.108	0.017	0.024	0.136	0.153
0-N2	0.124	0.016	0.020	0.110	0.162
0-N3	0.123	0.016	0.017	0.137	0.128
20-N0	0.118	0.020	0.028	0.185	0.192
20-N1	0.127	0.020	0.030	0.159	0.163
20-N2	0.123	0.018	0.026	0.179	0.152
20-N3	0.122	0.015	0.020	0.155	0.153
40-N0	0.128	0.016	0.024	0.228	0.195
40-N1	0.122	0.017	0.030	0.169	0.190
40-N2	0.121	0.020	0.022	0.248	0.212
40-N3	0.128	0.017	0.024	0.266	0.216
60-N0	0.125	0.020	0.023	0.296	0.222
60-N1	0.129	0.019	0.024	0.313	0.253
60-N2	0.131	0.018	0.026	0.228	0.252
60-N3	0.152	0.021	0.025	0.260	0.222
80-N0	0.152	0.043	0.042	0.335	0.232
80-N1	0.147	0.041	0.038	0.273	0.189
80-N2	0.170	0.040	0.048	0.285	0.242
80-N3	0.161	0.048	0.043	0.264	0.261
Mean for FYM doses (Factor A)					
0	0.118	0.016	0.021	0.130	0.149
20	0.122	0.018	0.026	0.170	0.165
40	0.125	0.018	0.025	0.228	0.203
60	0.134	0.020	0.025	0.274	0.237
80	0.157	0.043	0.042	0.289	0.231
Mean for N doses (Factor B)					
0	0.128	0.023	0.028	0.236	0.199
N1	0.126	0.023	0.029	0.210	0.190
N2	0.134	0.022	0.030	0.210	0.204
N3	0.137	0.027	0.028	0.216	0.196
LSD$_{0.05}$	A – 0.004 B – 0.003 A/B – 0.008 B/A – 0.007	A – 0.008 B – n.s. A/B – 0.015 B/A – 0.014	A – 0.005 B – n.s. A/B – 0.009 B/A – 0.009	A – 0.030 B – 0.025 A/B – 0.060 B/A – 0.056	A – 0.006 B – 0.005 A/B – 0.012 B/A – 0.011

n.s. – not significant.

Se content increased on average above 2-times against the control. The application of nitrogen decreased the selenium content in the investigated parts of spring barley in comparison with plants from plots without nitrogen fertilization.

The value of *bioaccumulation coefficient* (BC) reflects plant capacity for the nutrients uptake from soil and informs about the amount and the rate of the nutrient translocation from soil solution to aboveground plant parts [12]. The parameter is a ratio of the element concentration in plant aboveground parts or roots to its amount in soil. The bioaccumulation coefficients (BC) ratio calculated for the investigated parts of spring barley increased with increasing doses of FYM, but the FYM application at the dose of 80 Mg · ha^{-1} caused that aboveground parts and roots absorbed selenium more difficultly (Fig. 1).

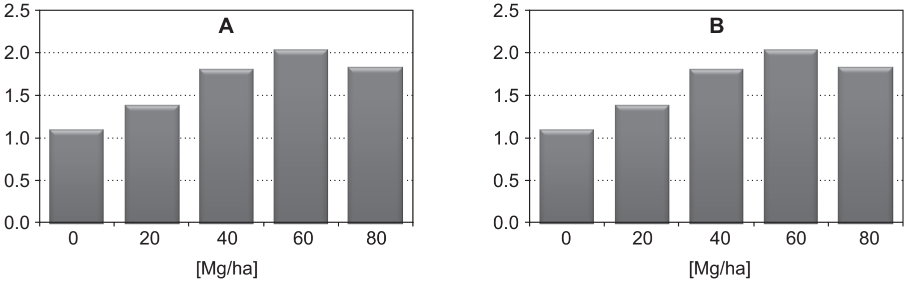

Fig. 1. Bioaccumulation coefficients (BC) for aboveground parts (A) and roots (B) of spring barley (mean for nitrogen doses)

The value of *translocation coefficient* (TC) informs about the amount and the rate of element translocation from roots to plant aboveground parts. The parameter is a ratio of the element concentration in aboveground plant parts to its amount in roots. The ratio values of TC increased with increasing doses of FYM (Fig. 2). According to Terry et al [13] the translocation of Se from root to shoot depends on the form of Se supplied, selenate being transported much more easily than selenite. Munier-Lamy et al [12] and Zhu et al [14] observed the differences in transporting Se from roots to shoots between plant species, which could be related either to the root system, *ie* to soil exploration by roots and root exudation, or to the chemical conditions resulting of microbial activity in

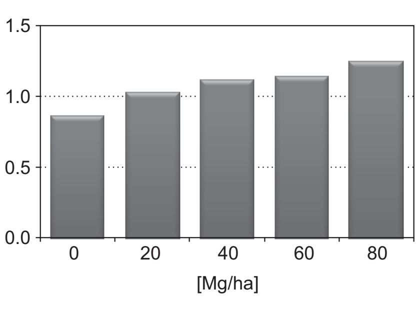

Fig. 2. Translocation coefficients (TC) for spring barley plants (mean for nitrogen doses)

the rhizosphere. Indeed, some microorganisms may excrete organic compounds that increase bioavailability, and facilitate root absorption of essential metals, such as Fe as well as non-essential metals, such as Cd. Soil microorganisms can also affect metal solubility directly by changing their chemical forms. In a pot experiment with barley [15] in which combined influence of N, P and S on the uptake of selenite was examined, a complex interaction between the three fertilizer anions and the plant uptake of selenite was revealed. Nitrogen application decreased the selenium concentration, which was to some extent only a dilution effect due to increase in yield. The decreasing effect of nitrogen fertilizer on selenium concentration was also found in pasture samples.

Conclusions

Comparison of the results of total soil Se concentration reported in this paper with other findings indicated that analysed soil had a very low selenium content. Such low levels of selenium in soils indicated that plants growing on these soils are deficient in this microelement. The application of manure and nitrogen resulted in the highest amounts of total selenium content in soil, which increased with increasing doses of both fertilizers. Fertilization with manure resulted in an increase of selenate(VI) and selenite(IV) in soil with increasing doses of manure, but the nitrogen treatment did not effect on the content of this fractions of selenium in soil. The share of Se-phytoavailable fractions in the total selenium content in soil under study ranged 13.5–27.3 % and increased with increasing doses of FYM. Generally, the selenium concentrations in aboveground parts and roots of spring barley increased with increasing doses of FYM, but the application of nitrogen decreased the Se content in the investigated parts of plants.

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WPŁYW NAWOŻENIA OBORNIKIEM I ZRÓŻNICOWANYMI DAWKAMI AZOTU NA PRZYSWAJALNOŚĆ SELENU PRZEZ JĘCZMIEŃ JARY (*Hordeum vulgare* L.)

Katedra Biochemii, Wydział Rolnictwa i Biotechnologii
Uniwersytet Technologiczno-Przyrodniczy w Bydgoszczy

Abstrakt: Celem badań było określenie zawartości selenu i jego frakcji fitodostepnych w glebie oraz przyswajalności tego pierwiastka przez jęczmień jary w warunkach nawożenia organiczno-mineralnego. Próbki glebowe i roślinne pobrano w maju 2003 roku (6 rotacja) w trakcie wegetacji jęczmienia jarego z doświadczenia prowadzonego przez IUNG w Puławach na terenie RZD Grabów nad Wisłą, z wariantu z następującym doborem roślin w zmianowaniu: ziemniaki – pszenica + międzyplon (gorczyca biała) – jęczmień jary + wsiewka koniczyny – koniczyna + trawy. Zastosowano nawożenie obornikiem (jednorazowo w trakcie rotacji) pod ziemniaki w dawkach 0, 20, 40, 60, 80 Mg · ha^{-1} oraz azotem w ilości 0, 40, 80 i 120 kgN · ha^{-1}. Zawartość selenu ogółem w próbkach roślinnych i glebowych oznaczono metodą Watkinsona. Zawartość Se(VI) i Se(IV) oznaczono, wykorzystując część analizy specjacyjnej wg Chao i Sanzolone w modyfikacji Wang i Chen. Zawartość selenu ogółem w glebie wskazuje, że była ona uboga w ten pierwiastek. Zastosowanie obornika i azotu spowodowało istotny wzrost zawartości selenu ogółem w glebie wraz ze wzrostem ich dawek. Udział frakcji fitoprzyswajalnych w całkowitej puli tego pierwiastka w glebie kształtował się od 13,5 do 27,3 % i wzrastał wraz ze wzrostem dawek obornika. Na ogół zawartość selenu w częściach nadziemnych i korzeniach jęczmienia jarego wzrastała wraz ze zwiększaniem się dawek obornika, natomiast zastosowanie azotu obniżyło zawartość tego mikroelementu w badanych częściach roślin.

Słowa kluczowe: selen, jęczmień jary, obornik, nawożenie azotem

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Anna PŁAZA[1], Feliks CEGLAREK, Barbara GĄSIOROWSKA,
Milena Anna KRÓLIKOWSKA and Małgorzata PRÓCHNICKA

INFLUENCE OF UNDERSOWN CROPS ON MINERAL NITROGEN CONTENT DETERMINED IN THE SOIL PROFILE IN AUTUMN AND IN SPRING IN CONVENTIONAL AND ORGANIC FARMING SYSTEMS

WPŁYW WSIEWEK MIĘDZYPLONOWYCH NA ZAWARTOŚĆ AZOTU MINERALNEGO OZNACZONEGO W GLEBIE JESIENIĄ I WIOSNĄ W KONWENCJONALNYM I EKOLOGICZNYM SYSTEMIE PRODUKCJI

Abstract: The aim of researches was to determine the influence of undersown crops plowed down in the autumn and left till spring in the form of mulch on mineral nitrogen content in the soil profile determined in autumn and in spring in conventional and organic farming systems.

The field experiments were conducted at the Zawady Experimental Farm owned by the University of Natural Sciences and Humanities in Siedlce. The following treatments were examined: factor 1 – Undersown crop: control object (no undersown crop cultivation), an undersown crop – biomass ploughed down in autumn (white melilot, white melilot + westerwold ryegrass, westerwold ryegrass), an undersown crop with its biomass used as a spring-incorporated mulch (white melilot, white melilot + westerwold ryegrass, westerwold ryegrass). factor 2 – farming system: conventional and organic. Ammonium and nitrate nitrogen contents were determined in two soil layers (0–30 and 31–60 cm) twice, *ie* in autumn and spring. The results showed that the highest soil concentrations of ammonium and nitrate ions were determined on control object, and in spring following white melilot incorporation.

The autumn and spring-determined soil contents of mineral nitrogen were significantly higher in the conventional in comparison with organic farming system. Mulching of the soil surface with undersown crops significantly reduced the mineral nitrogen content in soil in spring compared with the autumn-incorporated undersown crops.

Keywords: mineral nitrogen, soil, undersown crop, mulch, farming system

An assessment of mineral nitrogen content in soil has been assumed to be an indicator of environmental risk due to an excess concentration of nitrogen in the soil.

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[1] Department of Plant Cultivation, Siedlce University of Natural Sciences and Humanities, ul. B. Prusa 14, 08–110 Siedlce, Poland, phone: +48 25 643 12 81, email: plaza@uph.edu.pl

Catch crops are thus used as “accumulators” of the nutrients unused by the plants proceeding in the rotation. Leaching of nutrients into ground waters from plant-covered or mulched soils is much lower compared with “black” fallow [1–5]. Suggestions are also made to leave catch crops on the soil surface as mulch over the winter months [3, 6, 7]. There is still a paucity of experimental data on the topic, however. As a result, a need arises to continue studies to determine the effect of undersown crops autumn-incorporated or left as mulch till spring on mineral nitrogen contents determined in the soil profile in autumn and spring in the conventional and organic farming system.

Material and methods

Field studies were conducted in the years 2005–2008 at the Experimental Farm in Zawady owned by the University of Natural Sciences and Humanities in Siedlce. The experimental soil was Stagnic luvisol. The pH in KCl of the topsoil ranged between 6.4 and 6.5 and the soil contained 0.689–0.691 g $\cdot$ kg^{-1} N$_{tot}$, including 4.45–4.47 mg $\cdot$ kg^{-1} N-NH$_4$ and 7.25–7.27 mg $\cdot$ kg^{-1} N-NO$_3$, and the following available forms: P, K and Mg at the respective amounts of: 50.6–50.7, 112.9–113.0, and 53.9–54.1 mg $\cdot$ kg^{-1} [8]. The experiment was established as a split-blocks design with three replications. The following treatments were examined: factor 1 – Undersown crop: control object (no undersown crop cultivation), an undersown crop – biomass ploughed down in autumn (white melilot 26 kg $\cdot$ ha^{-1}, white melilot + westerwold ryegrass 13 + 10 kg $\cdot$ ha^{-1}, westerwold ryegrass 20 kg $\cdot$ ha^{-1}), an undersown crop with its biomass used as a spring-incorporated mulch (white melilot 26 kg $\cdot$ ha^{-1}, white melilot + westerwold ryegrass 13 + 10 kg $\cdot$ ha^{-1}, westerwold ryegrass 20 kg $\cdot$ ha^{-1}). factor 2 – farming system: conventional and organic.

Spring triticale grown for grain was undersown with the aforementioned crops. Prior to the experiment set-up, mineral fertilizers were applied in the conventional farming system at the following rates: 60 kg N, 39.6 kg P and 99.6 kg K per l ha. In the organic system, instead of mineral fertilization, farmyard manure was applied at the rate of 30 Mg (ton) $\cdot$ ha^{-1} taking into consideration the fertilizer needs of potato which was to follow the undersown crops. Both spring triticale and undersown crops were planted in early April. Spring triticale was harvested in early August.

After the harvest of spring triticale nitrogen fertilization was applied into the plots under westerwold ryegrass at the rate of 60 kgN $\cdot$ ha^{-1}, and the mixture of white melilot and westerwold ryegrass at the rate of 30 kgN $\cdot$ ha^{-1} .The control was tilled (to maintain “black” soil) from the harvest of spring triticale to late autumn. Soil samples were collected from two soil layers (0–30 and 31–60 cm) twice, that is in autumn (late October) and the next spring (early April). The ammonium and nitrate nitrogen contents were determined by colorimetric method [8]. All the characteristics studied were subjected to split-block variance analysis. When sources of variation were declared significant by analysis of variance, Tukey’s test was used to separate means.

Results and discussion

Autumn-determined mineral nitrogen content in the soil profile was significantly affected by the experimental factors and their interaction (Table 1 and 2).

Table 1

Soil N-NH$_4^+$ content determined in autumn, mg · kg^{-1} d.m. soil (means for 2005–2007)

Undersown crop	Farming system				Means	
	Conventional		Organic			
	Soil layer [cm]					
	0–30	31–60	0–30	31–60	0–30	31–60
Control object	4.86	2.43	3.93	1.85	4.40	2.14
White melilot	2.21	1.45	2.01	1.23	2.11	1.34
White melilot + westerwold ryegrass	1.78	1.31	1.53	1.12	1.66	1.22
Westerwold ryegrass	1.32	1.15	1.03	0.99	1.18	1.07
White melilot – mulch	2.19	1.44	1.99	1.21	2.09	1.33
White melilot + westerwold ryegrass – mulch	1.79	1.32	1.54	1.11	1.67	1.22
Westerwold ryegrass – mulch	1.34	1.16	1.05	0.98	1.20	1.07
Means	2.21	1.47	1.87	1.21	2.04	1.34
LSD$_{0.05}$						
Undersown crop					0.21	0.12
Farming system					0.19	0.16
Interaction					0.25	0.22

Table 2

Soil N-NO$_3^-$ content determined in autumn, mg · kg^{-1} d.m. soil (means for 2005–2007)

Undersown crop	Farming system				Means	
	Conventional		Organic			
	Soil layer [cm]					
	0–30	31–60	0–30	31–60	0–30	31–60
Control object	7.26	4.83	6.29	3.92	6.78	4.38
White melilot	4.89	2.41	4.21	2.00	4.55	2.21
White melilot + westerwold ryegrass	4.21	2.15	3.61	1.63	3.91	1.89
Westerwold ryegrass	3.50	1.85	2.99	1.24	3.25	1.55
White melilot – mulch	4.88	2.39	4.18	1.97	4.53	2.18
White melilot + westerwold ryegrass – mulch	4.20	2.14	2.62	1.62	3.41	1.88
Westerwold ryegrass – mulch	3.51	1.87	3.03	1.26	3.27	1.57
Means	4.64	2.52	3.85	1.95	4.24	2.24
LSD$_{0.05}$						
Undersown crop					0.28	0.22
Farming system					0.54	0.43
Interaction					0.61	0.47

The highest soil mineral nitrogen content was recorded in the control with no undersown crops. This is in agreement with the results reported by Fotyma [9] as well as Nowakowski and Kruger [4] who demonstrated that in autumn, when vegetation has ceased due to diminished nitrogen uptake and organic nitrogen mineralization, mineral nitrogen content in soil may increase. In this study inclusion of undersown crops into the cropping system, particularly westerwold ryegrass which is a non-leguminous plant, significantly reduced the soil mineral nitrogen content. The content was also significantly lower in the plots under the mixture of white melilot and westerwold ryegrass, compared with the control, though higher than under westerwold ryegrass. There was a clear reduction in soil mineral nitrogen content determined in late autumn following cultivation of undersown crops although is was definitely lower than the values reported elsewhere [10–12]. The possible explanation is that the soil nitrogen reservoir following cereals is large under intensive farming conditions, hence a greater influence of the catch crop. In the present study a higher soil nitrogen concentration was determined in the conventional versus organic farming system. Studies by Halberg et al [13], Werff et al [14] and Jonczyk [15] showed that the conventional farming system is characterized by excessive nitrogen which is used less efficiently. In this study there was found an interaction indicating that the highest soil mineral nitrogen content was in the control treatment where no undersown crop had been cultivated in the conventional farming system, and the lowest in the organic treatment under westerwold ryegrass. Similar findings were reported by Halberg et al [13] as well as by Duer [6].

An analysis of mineral nitrogen content in two soil layers in the study discussed here revealed that there was a clearly higher nitrogen concentration in the topsoil compared with the subsoil. It agrees with the results reported by Kus and Jonczyk [2]. Similarly to Sainju et al [16] and Trawczynski [17], the present work demonstrated a higher nitrate versus ammonium nitrogen content in the two soil layers. In autumn, the concentration of both the ions was the highest in both the soil layers of the control. Cultivation of undersown crops was followed by a significant reduction in $N\text{-}NH_4^+$ and $N\text{-}NO_3^-$ contents compared with their concentrations recorded in the two soil layers in the control with no undersown crops. The lowest ammonium and nitrate N contents were determined in the topsoil and subsoil following westerwold ryegrass, which agrees with the results reported by Breland [18] and Plaza et al [19].

The statistical analysis revealed a significant influence of the experimental factors together with their interaction on mineral nitrogen content in the soil profile in the spring (Table 3 and 4). Cultivation of undersown crops leads to significant increase of mineral nitrogen content in the topsoil, particularly following the incorporation of white melilot. This beneficial influence, that is stimulation of the process of organic nitrogen mineralization, is called the “priming effect” [16, 20, 21]. A significantly lower content of mineral nitrogen in soil, although higher than after westerwold ryegrass, was recorded following white melilot left as mulch till spring. The lowest mineral nitrogen concentration in the soil was determined in the treatment under westerwold ryegrass left on the soil surface over autumn and winter and incorporated in spring. According to Kus and Jonczyk [2], Nowakowski and Kruger [4] as well as Sanju and Sangh [21], the biomass of catch crop left on the soil surface decomposes more slowly than when ploughed in. In the present study it was demonstrated that, with adoption of this solution, there is potentially less risk of nitrogen loss from the soil over autumn and winter.

Table 3

Soil N-NH_4^+ content determined in spring, mg · kg^{-1} d.m. soil (means for 2006–2008)

Undersown crop	Farming system				Means	
	Conventional		Organic			
	Soil layer [cm]					
	0–30	31–60	0–30	31–60	0–30	31–60
Control object	5.44	3.95	4.30	2.71	4.87	3.33
White melilot	7.24	2.88	6.68	2.40	6.96	2.64
White melilot + westerwold ryegrass	6.57	2.54	6.23	2.24	6.40	2.39
Westerwold ryegrass	5.87	2.18	5.74	2.05	5.81	2.12
White melilot – mulch	6.56	2.35	6.15	2.01	6.36	2.18
White melilot + westerwold ryegrass – mulch	6.15	2.24	5.82	1.71	5.99	1.98
Westerwold ryegrass – mulch	5.71	2.09	5.45	1.37	5.58	1.73
Means	6.22	2.60	5.77	2.07	6.00	2.34
$LSD_{0.05}$						
Undersown crop					0.22	0.19
Farming system					0.20	0.17
Interaction					0.29	0.24

Table 4

Soil N-NO_3^- content determined in spring, mg · kg^{-1} d.m. soil (means for 2006–2008)

Undersown crop	Farming system				Means	
	Conventional		Organic			
	Soil layer [cm]					
	0–30	31–60	0–30	31–60	0–30	31–60
Control object	8.90	6.89	7.79	5.82	8.35	6.36
White melilot	19.41	5.87	17.33	3.72	18.37	4.80
White melilot + westerwold ryegrass	16.69	4.90	14.88	3.36	15.79	4.13
Westerwold ryegrass	13.94	3.88	12.38	2.97	13.16	3.43
White melilot – mulch	15.24	4.21	14.89	3.11	15.07	3.66
White melilot + westerwold ryegrass – mulch	13.83	3.62	12.59	2.64	13.21	3.13
Westerwold ryegrass – mulch	12.38	2.97	10.25	2.13	11.32	2.55
Means	14.34	4.62	12.87	3.39	13.61	4.01
$LSD_{0.05}$						
Undersown crop					1.31	0.22
Farming system					1.12	0.17
Interaction					1.73	0.32

The lowest mineral nitrogen content in the topsoil was measured in the control. Also, the farming system significantly influenced the mineral nitrogen concentration in the soil. The highest ammonium and nitrate nitrogen contents were recorded in the conventional farming system, the finding previously reported by Halberg et al [13] and Jonczyk [15]. There was found an interaction between the experimental factors in the trial discussed, which revealed the highest mineral nitrogen content in the topsoil after autumn-incorporated white melilot in the conventional farming system, and the lowest in the control in the organic farming system.

Analysis of mineral nitrogen content in soil showed a higher concentration of nitrate versus ammonium ions both in autumn and spring. This is in agreement with the results of studies reported by Moler and Stinner [20] and Sainju et al [16]. The subsoil mineral nitrogen content in the present study was the highest in the control, and the lowest after westerwold ryegrass left on the soil surface as mulch until spring. It should be stressed that reduction of nitrogen losses in the soil by means of including undersown crops in both the conventional and organic farming systems has recently become an issue of special importance.

Conclusion

1. In the autumn the highest concentration of mineral forms was determined on control object, and in spring after white melilot ploughing.
2. The soil mineral nitrogen contents determined in autumn and spring were significantly higher in the conventional versus organic farming system.
3. Undersown crops left till spring in the form of mulch caused the decrease of mineral nitrogen content in spring in soil in comparison with undersown crops plowed down in autumn.
4. The topsoil was characterized by a higher ammonium and nitrate nitrogen contents compared with the subsoil.

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WPŁYW WSIEWEK MIĘDZYPLONOWYCH NA ZAWARTOŚĆ AZOTU MINERALNEGO OZNACZONEGO W GLEBIE JESIENIĄ I WIOSNĄ W KONWENCJONALNYM I EKOLOGICZNYM SYSTEMIE PRODUKCJI

Katedra Szczegółowej Uprawy Roślin
Uniwersytet Przyrodniczo-Humanistyczny w Siedlcach

Abstrakt: Celem przeprowadzonych badań było określenie wpływu wsiewek międzyplonowych przyoranych jesienią i pozostawionych do wiosny w formie mulczu na zawartość mineralnych form azotu oznaczonego w profilu glebowym jesienią i wiosną w konwencjonalnym i ekologicznym systemie produkcji. Badania polowe przeprowadzono w RSD w Zawadach należącej do Uniwersytetu Przyrodniczo-Humanistycznego w Siedlcach. W doświadczeniu badano dwa czynniki. I. Wsiewka międzyplonowa: obiekt kontrolny (bez uprawy wsiewki międzyplonowej), wsiewka międzyplonowa – biomasa przyorana jesienią (nostrzyk biały, nostrzyk biały + życica westerwoldzka, życica westerwoldzka), wsieka międzyplonowa – biomasa pozostawiona do wiosny w formie mulczu (nostrzyk biały, nostrzyk biały + życica westerwoldzka, życica westerwoldzka). II. System produkcji: konwencjonalny, ekologiczny. Zawartość jonów amonowych i azotanowych oznaczono dwukrotnie, tj. jesienią i wiosną, w dwóch warstwach gleby (0–30 i 31–60 cm). Otrzymane wyniki badań pozwalają stwierdzić, że jesienią najwyższą zawartość mineralnych form azotu odnotowano na obiekcie kontrolnym, a wiosną po przyoraniu nostrzyku białego. W konwencjonalnym systemie produkcji zawartość azotu mineralnego oznaczonego w glebie zarówno jesienią, jak i wiosną była istotnie wyższa niż w ekologicznym systemie produkcji. Wsiewki międzyplonowe pozostawione do wiosny w formie mulczu spowodowały zmniejszenie zawartości azotu mineralnego w glebie wiosną w porównaniu do wsiewek międzyplonowych przyoranych jesienią.

Słowa kluczowe: azot mineralny, gleba, wsiewka międzyplonowa, mulcz, system produkcji

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Antoni ROGÓŻ[1]

TRACE ELEMENT CONTENT IN CEREAL WEEDS AGAINST THE BACKGROUND OF THEIR SOIL CONTENTS PART 2. CHROMIUM AND LEAD CONTENTS IN SOIL AND WEEDS*

ZAWARTOŚĆ PIERWIASTKÓW ŚLADOWYCH W CHWASTACH ROŚLIN ZBOŻOWYCH NA TLE ICH ZAWARTOŚCI W GLEBIE Cz. 2. ZAWARTOŚĆ CHROMU ORAZ OŁOWIU W GLEBIE I CHWASTACH

Abstract: The investigations aimed at determining the contents of chromium and lead in weeds occurring in cereal crops, *ie* cornflower – *Centaurea cyanus* L., poppy – *Papaver rhoeas* L., corn chamomile – *Anthemis arvensis* L. and thistle – *Cirsium arvense* (L.) Scop. against the background of their soil contents. The soils, from which the materials for analyses were gathered, revealed a considerable diversification in these element contents, both in soluble forms assessed in 0.1 mol · dm^{-3} HCl solution and in approximate to total contents.

Total chromium and nickel contents in the studied soils ranged widely (14.44–58.30) mgCr · kg^{-1}, at geometric mean 24.72 mgCr · kg^{-1}, and from 17.34 mgPb · kg^{-1} to 30.44 mgPb · kg^{-1}, at geometric mean 25.53 mgPb · kg^{-1} of soil. Contents of chromium and lead soluble forms fluctuated from 0.11 mgCr · kg^{-1} to 0.39 mgCr · kg^{-1}, at geometric mean 0.21 mgCr · kg^{-1}, and from 3.88 mgPb · kg^{-1} to 10.11 mgPb · kg^{-1}, at geometric mean 7.25 mgPb · kg^{-1} of soil.

Chromium and lead contents in the studied weeds ranged widely depending on weed species, analyzed plant part, soil reaction and these elements concentrations in soil. Statistical analysis of the obtained results revealed that physicochemical properties of the analyzed soils not unanimously affected chromium and lead contents in the researched weeds.

Lead content was decreasing in the aboveground parts of the analyzed weeds with pH_{KCl} value increasing over 5.5, whereas in roots its contents changed irregularly. No unanimous influence of the soil reaction on chromium accumulation in the studied weeds was observed. In all analyzed weeds much higher contents of the discussed metals were assessed in roots than in the aboveground parts.

Keywords: weeds, chromium and lead concentrations, soil pH_{KCl}

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[1] Department of Agricultural and Environmental Chemistry, University of Agriculture in Krakow, al. A. Mickiewicza 21, 31–120 Kraków, Poland, phone: +48 12 662 43 48, fax: +48 12 662 48 41, email: rrrogoz@cyf-kr.edu.pl

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The natural environment pollution with trace metals leads to their increased contents in all biotic elements of ecosystems. The agroecosystems occurring in polluted areas face a hazard of excessive concentrations of heavy metals in plants designed for animal fodder or human food. Beside other quality parameters the excess of these metals in plants determines the quality of animal feeds or food products [1, 2].

Determining the level of heavy metals in crops cultivated in the areas threatened with anthropogenic pollution allows to organize farming in these areas towards diminishing negative effect of these elements through various agrotechnological measures, such as liming or increasing the contents of organic matter and proper selection of plants [1, 3]. The most frequently mentioned factors affecting heavy metal salts solubility in soil comprise: organic matter contents, soil granulometric composition, sorption capacity and soil pH [1, 4–7].

The investigations aimed at determining the contents of chromium and lead in weeds growing in cereal crops against the background of their soil concentrations.

Material and methods

Thirty soil samples were collected from the 0–25 cm layer of arable land on which cereal crops were cultivated in the Brzeznica commune in the first decade of June 2007. Each soil sample (0.5; 1.0) kg of soil was an average sample of individual ones. Basic physical and chemical properties were determined in the collected soil samples using agricultural chemistry standard methods [8]: granulometric composition was determined using Bouyoucose-Casagrande aerometric method modified by Proszyński, pH by potentiometric method in soil suspension in H_2O and 1 mol · dm^{-3} KCl solution, hydrolytic acidity by means of Kappen method and organic carbon content using Tiurin method.

Weeds growing in cereal crops, *ie* cornflower – *Centaurea cyanus* L., poppy – *Papaver rhoeas* L., corn chamomile – *Anthemis arvensis* L. and thistle – *Cirsium arvense* (L.) Scop. were collected from the same sites. The site where both soil and plant samples were collected was described in the "Materials and methods" section in the first part of the previous article [9].

Total contents of trace elements in the analyzed soils were determined following their mineralization at the temperature of 450 ^{o}C. Next, they were digested in a mixture of perchloric(VIII) and nitric(V) acid mixture (2 : 3, v/v). Mineralized soil material was dissolved in HCl [8]. The contents of trace elements in soluble forms were determined in 0.1 mol · dm^{-3} HCl solution, and the soil to extraction solution ratio was 1 : 10.

Collected plant material was washed, the samples were divided into the aerial parts and roots, dried, crushed and dry mineralized. The ash was dissolved in nitric acid (1 : 2). In the obtained solutions of the soil and plant samples chromium and lead contents were assessed using *atomic absorption spectrophotometry* (AAS). Obtained results of these elements contents in soil and analyzed weeds were elaborated statistically, *ie* arithmetic and geometric mean were calculated, as well as standard deviation and simple correlation coefficients.

Results and discussion

Characteristics of collected soil material

The analyzed soils were greatly diversified concerning their granulometric composition, soil pH, organic carbon content and the analyzed elements, both their soluble forms and approximate to total contents. The value of soil pH assessed in water suspension ranged from 4.81 to 7.68, whereas in 1 mol KCl · dm^{-3} solution from 3.95 to 6.64. The results of analyses of physicochemical soil properties were presented in the first part of the previous article [9].

Soil pH is one of the factors determining solubility of mineral compounds and therefore their availability to plants. Total chromium and nickel contents in the studied soils ranged widely from 14.44 mgCr · kg^{-1} to 58.30 mgCr · kg^{-1}, at geometric mean 24.72 mgCr · kg^{-1}, and from 17.34 mgPb · kg^{-1} to 30.44 mgPb · kg^{-1}, at geometric mean 25.53 mgPb · kg^{-1} (Table 1). In slightly acid and neutral soils total contents of chromium and lead were by 10 % lower in comparison with chromium and lead contents in soil with pH lower than 5.5.

Table 1

Chromium and lead content in soil, depending on soil reaction

Specification	Total content		Soluble forms content	
	[mg · kg^{-1}]			
	Cr	Pb	Cr	Pb
pH in 1 mol KCl · dm^{-3} ≤ 5.5				
Arithmetic mean	27.77	26.64	0.211	7.95
Geometric mean	**25.85**	**26.45**	**0.197**	**7.86**
Range	(14.44–58.30)	(17.30–30.44)	(0.11–0.391)	(5.80–10.11)
Relative standard deviation [%]	42	12	40	15
pH in 1 mol KCl · dm^{-3} from 5.5 to 6.5				
Arithmetic mean	23.22	24.63	0.238	6.38
Geometric mean	**22.90**	**24.34**	**0.234**	**6.21**
Range	(18.11–25.25)	(17.63–27.65)	(0.16–0.33)	(3.88–9.31)
Relative standard deviation [%]	17	15	20	15
pH in 1 mol KCl · dm^{-3} ≥ 6.6				
Arithmetic mean	22.19	24.66	0.257	7.21
Geometric mean	**22.18**	**24.52**	**0.236**	**7.13**
Range	(21.48–23.33)	(21.99–27.15)	(0.14–0.39)	(5.71–7.98)
Relative standard deviation [%]	5	13	70	18

The contents of soluble chromium and lead forms ranged widely: for chromium from 0.11 mgCr · kg^{-1} to 0.39 mgCr · kg^{-1}, at geometric mean 0.21 mgCr · kg^{-1}, whereas for lead from 3.88 mgPb · kg^{-1} to 10.11 mgPb · kg^{-1}, at geometric mean 7.25 mgPb · kg^{-1} (Table 1). The share of chromium and lead soluble forms in their total contents in the studied soils ranged from 0.52 % to 3.72 % for chromium and from 15 % to 39 % for lead.

Gasior et al [10] stated that the content of soluble element forms in soil after flood depended on percentage of floatable particles, soil pH and humus content.

It was revealed that at $pH_{KCl} > 5.5$ the amount of soluble lead forms diminished in the analyzed soils but opposite effect was observed for chromium which soluble forms contents increased under those conditions. In slightly acid and neutral soils soluble chromium content was by 19 % higher than in very acid soils with $pH_{KCl} \le 5.5$. Wisniowska-Kielian [11] revealed that mountain soils with higher sum of total precipitation (Tymbark commune) contained twice larger amounts of Pb, Cd and Cr but 20 % less of Ni in soluble forms than weakly acid soils from the lowland areas (Przemysl commune). Statistical analysis showed that physical, physicochemical and chemical properties of the studied soils not unanimously affected the contents of analyzed elements and their soluble forms, as evidenced by simple correlation coefficients (Table 2).

Table 2

Simple correlation coefficients (r) between chromium and lead contents in soil and selected soil properties

Soil properties n = 30	Total forms		Soluble forms	
	Cr	Pb	Cr	Pb
pH_{KCl} value	–0.129	–0.418*	0.419*	–0.457**
Content of C_{org} [%]	0.146	0.504**	0.183	0.318
Share of fraction with diameter:				
< 0.02 mm	0.354*	0.302	0.025	–0.060
< 0.002 mm	0.322	0.384*	–0.358*	0.037

n = number of samples 30; r significant at: *p = 0.05; **p = 0.01.

A significant positive dependence was demonstrated between soil pH assessed in KCl solution and soluble chromium form content, where the value of simple correlation coefficient for these parameters was $r = 0.419$; ($p < 0.01$), whereas a significantly negative dependence was registered for lead; $r = –0.425$; ($p < 0.01$). A significant positive relationship was revealed between organic carbon content and total lead content but also between the content of floatable particles and total content of analyzed cations (Table 2). Kalembasa et al [12] demonstrated significant positive dependencies between the contents of heavy metals and organic C content, sorption capacity (T) and the content of floatable particles in alluvial soils.

On the basis of obtained results the analyzed soils in which cereals were cultivated were assessed concerning the degree of pollution with lead and chromium according to the guidelines suggested by Kabata-Pendias et al [13]. It was revealed that all soil samples showed natural contents of these metals (0^o).

Contents of chromium and lead in plants

Contents of Cr and Pb in collected weeds from cereal crops ranged widely depending on: the species, analyzed plant part and soil reaction, contents of total and available forms of these elements in soil. The relationships were confirmed by numerous experiments [1, 14–16].

Chromium is an element necessary for growth and development of living organisms. The element is absorbed by plants passively, so its concentration in the individual plant parts is a derivative of its concentrations in the soil solution. It is the element responsible for many physiological processes and for activation of some enzymes in plants, particularly from the oxyreductase group.

Geometric mean contents of chromium in the roots of studied weeds from cereal crops was put in the following order according to increasing contents: poppy – 2.39 mgCr $\cdot$ kg^{-1}, thistle – 2.56 mgCr $\cdot$ kg^{-1}, corn chamomile – 3.66 mgCr $\cdot$ kg^{-1} and cornflower – 5.42 mgCr $\cdot$ kg^{-1}, whereas for the aboveground parts the order was as follows: thistle 1.95 mgCr $\cdot$ kg^{-1}, corn chamomile – 1.99 mgCr $\cdot$ kg^{-1}, poppy – 2.06 mgCr $\cdot$ kg^{-1} and cornflower – 2.94 mgCr $\cdot$ kg^{-1} (Table 3).

Table 3

Chromium and lead contents [mg $\cdot$ kg^{-1} d.m.] in cereal crop weeds
depending on soil reaction

Mean content	Roots		Aboveground parts	
	Cr	Pb	Cr	Pb
Cornflower – ***Centaurea Cyanus* L.**; n = 30				
pH in 1 mol KCl $\cdot$ dm^{-3} ≤ 5.5				
Arithmetic mean	6.61	3.09	3.64	1.30
Geometric mean	**5.87**	**2.99**	**3.13**	**1.22**
Range	(3.52–19.70)	(1.85–4.85)	(1.49–7.84)	(0.68–2.75)
pH in 1 mol KCl $\cdot$ dm^{-3} from 5.5 to 6.5				
Arithmetic mean	5.14	2.31	3.37	1.44
Geometric mean	**4.79**	**2.09**	**2.79**	**1.16**
Range	(2.89–10.25)	(1.24–5.33)	(1.16–2.46)	(0.59–3.51)
pH in 1 mol KCl $\cdot$ dm^{-3} ≥ 6.5				
Arithmetic mean	7.09	2.69	3.37	1.28
Geometric mean	**6.99**	**2.64**	**2.79**	**1.22**
Range	(6.18–8.84)	(1.88–3.09)	(1.16–7.94)	(0.89–1.85)
Poppy – ***Papaver rhoeas* L.**; n = 30				
pH in 1 mol KCl $\cdot$ dm^{-3} ≤ 5.5				
Arithmetic mean	2.79	1.47	2.64	1.18
Geometric mean	**2.65**	**1.37**	**2.37**	**1.04**
Range	(1.41–4.14)	(0.56–2.45)	(0.93–6.04)	(0.48–2.59)

Table 3 contd.

Mean content	Roots		Aboveground parts	
	Cr	Pb	Cr	Pb
pH in 1 mol KCl · dm^{-3} from 5.5 to 6.5				
Arithmetic mean	1.87	0.87	1.88	0.85
Geometric mean	**1.75**	**0.82**	**1.79**	**0.75**
Range	(1.12–4.22)	(0.52–1.30)	(1.31–3.50)	(0.28–1.37)
pH in 1 mol KCl · dm^{-3} from 5.5 to 6.5				
Arithmetic mean	2.58	1.05	1.73	0.87
Geometric mean	**2.56**	**1.00**	**1.70**	**0.83**
Range	(2.12–2.28)	(0.64–1.39)	(1.31–2.07)	(0.59–1.17)
Corn chamomile – *Anthemis arvensis* L.; n = 30				
pH in 1 mol KCl · dm^{-3} ≤ 5.5				
Arithmetic mean	4.79	2.90	2.53	1.28
Geometric mean	**4.41**	**2.04**	**2.35**	**1.18**
Range	(2.12–9.98)	(0.45–7.64)	(1.18–5.07)	(0.61–1.17)
pH in 1 mol KCl · dm^{-3} from 5.5 to 6.5				
Arithmetic mean	3.46	1.29	1.86	0.99
Geometric mean	**3.13**	**1.16**	**1.70**	**0.89**
Range	(1.79–7.25)	(0.45–2.07)	(0.87–3.04)	(0.46–2.14)
pH in 1 mol KCl · dm^{-3} from 5.5 to 6.5				
Arithmetic mean	2.36	1.96	1.52	0.76
Geometric mean	**2.32**	**1.35**	**1.49**	**0.74**
Range	(2.01–3.01)	(1.21–1.69)	(1.21–1.96)	(0.56–1.35)
Thistle – *Cirsium arvense* (L.) Scop.; n = 30				
pH in 1 mol KCl · dm^{-3} ≤ 5.5				
Arithmetic mean	2.74	2.26	1.92	1.53
Geometric mean	**2.59**	**1.91**	**1.75**	**1.31**
Range	(1.61–5.79)	(0.88–5.89)	(0.97–4.09)	(0.56–4.01)
pH in 1 mol KCl · dm^{-3} from 5.5 to 6.5				
Arithmetic mean	2.56	0.96	3.00	1.20
Geometric mean	**2.39**	**0.88**	**2.54**	**1.16**
Range	(1.39–4.06)	(0.35–1.42)	(1.27–7.14)	(0.71–1.66)
pH in 1 mol KCl · dm^{-3} ≥ 6.5				
Arithmetic mean	3.10	1.30	1.81	0.93
Geometric mean	**2.89**	**1.16**	**1.73**	**0.92**
Range	(1.65–3.83)	(0.72–2.16)	(1.15–2.39)	(0.77–1.07)

Lead uptake by plant roots is a passive process and proportional to the occurrence of its soluble forms in the substratum. Generally higher contents are assessed in plant roots than in the aerial parts. Geometric mean content of lead in the roots of the analyzed weeds from cereal crops was ordered according to increasing contents: poppy – 1.14 mgPb $\cdot$ kg^{-1}, thistle 1.34 mgPb $\cdot$ kg^{-1}, corn chamomile – 1.62 mgPb $\cdot$ kg^{-1} and cornflower – 2.62 mgPb $\cdot$ kg^{-1}, whereas in the aboveground parts respectively: poppy 0.91 mgPb $\cdot$ kg^{-1}, corn chamomile 1.02 mgPb $\cdot$ kg^{-1}, thistle 1.17 mgPb $\cdot$ kg^{-1} and cornflower 1.19 mgPb $\cdot$ kg^{-1}.

No unanimous effect of the studied soils reaction on chromium or lead contents in weeds from cereal crops was observed, except corn chamomile. Geometric mean contents of chromium and lead in the roots of corn chamomile from slightly acid and neutral soils was lower for chromium by 24 and 29 % and for lead by 44 and 8 %, respectively, in relation to geometric mean contents of these metals in corn chamomile roots from the soils with $pH_{KCl} \leq 5.5$ (Table 3). In the roots of cornflower growing in slightly acid soils chromium content was smaller by 19 %, whereas this metal contents in cornflower roots from neutral soils with $pH_{KCl} \geq 6.6$ was 19 % higher in comparison with cornflower roots gathered from very acid soils (Table 3). Wisniowska-Kielian [11] demonstrated that wheat roots from strongly acid soils contained three times larger amounts of Cd and Ni and twice more of Pb and Cr than the roots from less acidified soils.

Table 4

Values of simple correlation coefficients (r) between chromium and lead contents in cereal weeds and selected soil properties

Properties of soil	**Cornflower – *Centaurea Cyanus* L.**; n = 30			
	roots		aboveground parts	
	Cr	Pb	Cr	Pb
pH_{KCl} value	–0.1382	–0.5528*	–0.1558	0.0447
Total content	0.0563	0.3286	–0.0612	0.1623
Soluble forms	–0.1523	0.3683*	0.3081	0.0683
Poppy – *Papaver rhoeas* L.; n = 30				
pH_{KCl} value	–0.2528	–0.5428**	–0.3714*	–0.2299
Total content	0.0055	0.3133	–0.1288	–0.0058
Soluble forms	0.0597	0.5328**	0.3726*	0.1746
Corn chamomile – *Anthemis arvensis* L.; n = 30				
pH_{KCl} value	–0.4213*	–0.3417*	–0.3648*	–0.2063
Total content	0.1213	0.0103	0.1269	–0.1477
Soluble forms	–0.2763	0.0447	–0.3178	0.0664
Thistle – *Cirsium arvense* (L.) Scop.; n = 30				
pH_{KCl} value	0.0686	–0.3752*	0.1512	–0.0948
Total content	0.2720	0.3274	–0.3333	–0.2482
Soluble forms	0.1428	0.3303	0.0553	0.0767

n = number of plant samples 30; r significant at: *p = 0.05;**p = 0.01.

Statistical analysis of the obtained results showed that physicochemical properties of the analyzed soils not unanimously affected chromium and lead contents in weeds from cereal crops, as evidenced by simple correlation coefficients (Table 4). Significantly negative relationship was demonstrated between pH value of the studied soils and lead contents in the roots of the analyzed weeds (Table 4).

Chromium and lead contents both in roots and the aboveground parts of the analyzed weeds from cereal crops were small and no exceeded critical values of these elements concentrations were assessed in plants designed for animal feeds [13]. It suggests that no exceeded critical concentrations of these elements occur in the cultivated cereal crops.

Conclusions

1. Analyzed soils revealed a considerable diversification concerning their approximate to total contents of the studied elements and their soluble forms. In very acid soils higher contents of these elements were assessed in comparison with slightly acid and alkaline soils. All studied soils had natural contents of these elements.
2. The contents of chromium and lead in the researched weeds ranged widely depending on the weed species, analyzed plant part, soil pH and content of these elements soluble forms in soil. Much higher contents were assessed in the roots than in the aboveground parts.
3. No exceeded critical contents of chromium or lead were revealed in the roots or the aboveground parts of the analyzed weeds. It may suggest a good quality of cultivated cereals since no critical concentrations of these metals occurred.

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ZAWARTOŚĆ PIERWIASTKÓW ŚLADOWYCH W CHWASTACH ROŚLIN ZBOŻOWYCH NA TLE ICH ZAWARTOŚCI W GLEBIE
Cz. 2. ZAWARTOŚĆ CHROMU ORAZ OŁOWIU W GLEBIE I CHWASTACH

Katedra Chemii Rolnej i Środowiskowej
Uniwersytet Rolniczy im. Hugona Kołłątaja w Krakowie

Abstrakt: Celem badań było określenie zawartości chromu i ołowiu w chwastach występujących w uprawach roślin zbożowych, tj.: chaber bławatek – *Centaurea cyanus* L., mak polny – *Papaver rhoeas* L., rumian polny – *Anthemis arvensis* L. oraz ostrożeń polny – *Cirsium arvense* (L.) Scop. na tle ich zawartości w glebie. Gleby, na których zebrano materiał do badań, cechowały się znacznym zróżnicowaniem pod względem zawartości tych pierwiastków, zarówno w formach rozpuszczalnych oznaczonych w roztworze HCl o stężeniu 0,1 mol $\cdot$ dm^{-3}, jak i formach zbliżonych do całkowitych zawartości.

Całkowita zawartość chromu i ołowiu w badanych glebach wahała się w szerokim zakresie: dla chromu od 14,44 do 58,30 mgCr $\cdot$ kg^{-1}, ze średnią geometryczną 24,72 mgCr $\cdot$ kg^{-1}, natomiast dla ołowiu od 17,34 mgPb $\cdot$ kg^{-1} do 30,44 mgPb $\cdot$ kg^{-1}, ze średnią geometryczną 25,53 mgPb $\cdot$ kg^{-1}. Zawartość chromu i ołowiu w formach rozpuszczalnych wahała się w zakresie: dla chromu od 0,11 mgCr $\cdot$ kg^{-1} do 0,39 mgCr $\cdot$ kg^{-1}, ze średnią geometryczną 0,21 mgCr $\cdot$ kg^{-1}, natomiast dla ołowiu od 3,88 mgPb $\cdot$ kg^{-1} do 10,11 mgPb $\cdot$ kg^{-1}, ze średnią geometryczną 7,25 mgPb $\cdot$ kg^{-1}.

Zawartość chromu i ołowiu w zebranych chwastach wahała się w szerokim zakresie w zależności od: gatunku chwastu, analizowanej części rośliny, odczynu gleby i zawartości tych pierwiastków w glebie. Analiza statystyczna uzyskanych wyników wykazała, że właściwości fizykochemiczne badanych gleb w niejednakowym stopniu wpływały na zawartość chromu i ołowiu w badanych chwastach.

Wraz ze wzrostem wartości pH$_{\mathrm{KCl}}$ powyżej 5,5 zawartość ołowiu w częściach nadziemnych badanych chwastów zmniejszała się, natomiast w korzeniach jego zawartość zmieniała się w sposób nieregularny. Nie zaobserwowano jednoznacznego wpływu odczynu gleby na akumulację chromu w badanych chwastach. We wszystkich badanych chwastach stwierdzono znacznie wyższe zawartości badanych metali w korzeniach niż częściach nadziemnych.

Słowa kluczowe: chwasty, zawartość chromu i ołowiu, pH$_{\mathrm{KCl}}$ gleby

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Magdalena KRZYŻANIAK-SITARZ[1]

INFLUENCE OF GRADUATION TOWERS ON AVERAGE ANNUAL CATIONS CONTENT IN BLACK EARTHS (MOLLIC GLEYSOLS) IN THE INOWROCLAW CITY

WPŁYW TĘŻNI NA WARTOŚCI ŚREDNIOROCZNE KATIONÓW W CZARNYCH ZIEMIACH W INOWROCŁAWIU

Abstract: The research concerns soils located in the Inowroclaw Spa Park, under continuous influence of graduation towers. Such a continuous impact of aerosols may modify chemical composition of soils, and may lead to transformation of black earths into salt-affected anthropogenic soils in the nearest future. This specific anthropogenic factor effected the increase of calcium and sodium cations content, significantly changing the composition of soil sorption complex of the analyzed soils. The results of separate cations content in sorption complex showed the domination of calcium cations (91.42–333.35 $\mathrm{mmol \cdot kg^{-1}}$), which in several soil profiles attained a two or even three times higher value than in Cuiavian black earths under no anthropogenic influence. Sodium came second in content series of cations (16.28–73.46 $\mathrm{mmol \cdot kg^{-1}}$). In most of the horizons of the investigated soils the content of these exchangeable cations was on average level. It means that the content of sodium cations was several times higher than in the black earths not affected by salt, yet lower than in soils under the influence of sodium industry. The rest of the analyzed cations (Mg^{2+}, K^{+}) were characterized by low concentration both in soil sorption complex and in the soil solution and did not show accumulation characteristics in any genetic horizons.

Keywords: black earth, physical and chemical properties, anthropopressure, graduation tower

Soils of the Spa Park in Inowroclaw, as most Inowroclaw Plain's soils, belong to one of the largest black earths (Mollic Gleysols) complex in Poland [1]. The black earths are characterised by high amount of organic matter and content of calcium carbonate. Their high cation exchange capacity is effected by high concentration of calcium and magnesium cations and lower potassium concentration. The black earths richness in alkaline cations influences these soils' reaction and low concentration of hydrogen cations in sorption complex. On account of its location and agricultural usefulness, the

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[1] Department of Environmental Development and Protection, University of Technology and Life Sciences in Bydgoszcz, ul. Sucha 7, 85–791 Bydgoszcz, Poland, phone: +52 340 84 40, fax: +52 340 81 41, email:sitmag@wp.pl

area of black earths in Kujawy is exposed to considerable human impact, the consequence of which are changes in physicochemical properties of the soil. The most spectacular phenomenon of those soils' degradation is the salinity process. Natural salinity in Poland has a low range, and because of that the human activity is thought to be the main cause of that phenomenon, especially the impact of the sodium and mining industry, soil irrigation with sewage, the usage of mineral fertilizers, and deicing agents on roads. The unique factor occurring in the Spa Park in Inowroclaw and affecting the soils' chemical composition are graduation towers. Graduation towers effect appearance of halophytic plants or dying off of trees and bushes poorly selected for the spa area. Moreover, the salinity process is not only the problem of spatial adaptation of the investigated area. The long-term influence of aerosols hanging over the graduation towers can modify the chemical composition of the soils, up to the point that in the nearest future, they might stop existing as black earths and become saline-sodic soils or anthropogenic saline soils.

The objective of this research was to define the impact of graduation towers on changeability of the composition of the sorption complex and soil solution of the Inowroclaw Spa Park's soils.

Material and methods of research

The area of the research covers almost 60 hectares of the Spa Park in Inowroclaw. In the Park's area, three times during the year (Spring, Summer, Autumn) soil profiles from seven research points were identified (Fig. 1). From each of the genetic horizons

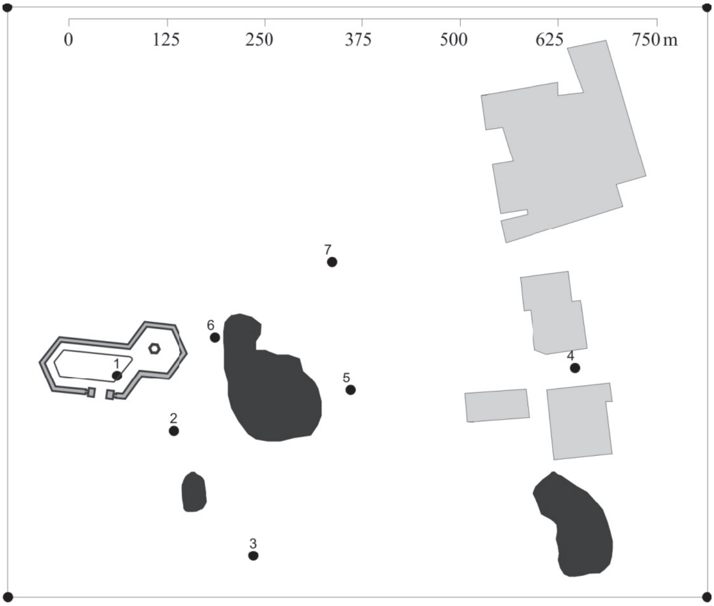

Fig. 1. Location of soil profiles

of soil profiles samples were taken to laboratory analyses. The following soil parameters were determined using widely applied methods in the soil science:

– exchangeable cations (Ca, Mg, Na, K) in 1M NH_4Cl of pH 8,2 using AAS method;

– water-soluble forms Ca, Mg, K, Na using AAS method;

– sorption capacity and a degree of a saturation of a sorption complex, which was determined mathematically.

Findings of the aspirated air quality measurements near the graduation towers collected in the development of the National Hygiene Institute in Poznan indicates that the dominating aerosol's compound produced by the graduation towers is sodium chloride 0.79–95.96 $mg \cdot m^{-3}$. The content of the sodium chloride is diversified and depended on the distance from the graduated towers and the altitude above the ground level. The efficiency of brine pumps in graduation towers also have essential influence on aerosol concentration, technical condition of graduation towers, concentration and composition of brine (Table 1), and atmospheric factors – especially wind direction and speed. The highest concentration of NaCl was observed in the vicinity of fountain and pumping station, the lowest on graduation tower deck [2].

Table 1

Brine composition

Parameter	Brine pumped to graduation towers	Brine after distribution through the system
pH	7.8	7.5
Cations		
Na^+	18160.00 $mg \cdot dm^{-3}$	21530.00 $mg \cdot dm^{-3}$
Ca^{2+}	424.85 $mg \cdot dm^{-3}$	464.93 $mg \cdot dm^{-3}$
Mg^{2+}	228.47 $mg \cdot dm^{-3}$	175.00 $mg \cdot dm^{-3}$
Anions		
Cl^-	28000 $mg \cdot dm^{-3}$	33200 $mg \cdot dm^{-3}$
I^-	2.1 $mg \cdot dm^{-3}$	2.3 $mg \cdot dm^{-3}$
HCO_3^-	414.93 $mg \cdot dm^{-3}$	463.74 $mg \cdot dm^{-3}$
NO_2^-	0.38 $mg \cdot dm^{-3}$	0.48 $mg \cdot dm^{-3}$
NO_3^-	n.s.	n.s.
SO_4^{2-}	1341.49 $mg \cdot dm^{-3}$	1316.80 $mg \cdot dm^{-3}$
NaCl	46160 $mg \cdot dm^{-3}$	54730 $mg \cdot dm^{-3}$
Total	48572.20 $mg \cdot dm^{-3}$	57152.22 $mg \cdot dm^{-3}$

n.s. – non significant.
Results of National Institute of Hygiene in Poznan [2].

Results and discussion

On the basis of the results published earlier [3], soils of the Spa Park in Inowroclaw were classified as black earths (Mollic Gleysols). The analysis of separate cations in sorption complex showed the dominance of calcium cations 91.42–333.35 $mmol \cdot kg^{-1}$, with specific differences in concentration of these cations in individual genetic horizons of investigated soil profiles (Table 2).

Table 2

The content of exchangeable and watersoluble cation forms in studied soils

Profile No.	PWK CEC	Ca^{2+} exch	Mg^{2+} exch	Na^{+} exch	K^{+} exch	H^{+} exch	Ca^{2+} wslb	Mg^{2+} wslb	Na^{+} wslb	K^{+} wslb
	$mmol \cdot kg^{-1}$									
Profile 1										
0–20	277.06	220.29	10.85	41.64	4.28	0.00	1.04	1.17	14.51	0.69
20–40	248.00	190.18	10.57	43.93	3.32	0.00	0.26	1.12	17.52	0.73
40–60	197.21	130.13	7.52	56.31	3.25	0.00	0.12	1.43	26.22	1.10
110–130	172.06	91.54	4.85	72.79	2.88	0.00	0.09	1.63	30.00	1.19
130–150	249.60	168.45	4.66	73.46	3.03	0.00	0.20	2.04	31.64	1.78
Profile 2										
0–20	201.01	162.28	12.93	17.65	8.15	0.00	0.92	1.33	1.57	2.12
20–40	179.24	145.04	11.16	19.89	3.15	0.00	0.64	1.19	1.55	0.26
40–60	200.94	168.09	10.17	20.05	2.63	0.00	0.39	1.20	3.25	0.41
82–107	226.49	181.04	12.40	30.31	2.74	0.00	0.39	0.99	7.07	0.62
107–150	358.03	307.00	15.15	32.97	2.91	0.00	4.31	0.70	10.65	0.34
Profile 3										
0–20	192.08	130.41	10.22	24.79	4.76	21.90	0.36	0.91	0.85	1.45
20–40	199.71	154.66	9.38	18.94	3.30	13.43	0.07	0.94	1.24	0.44
40–55	255.49	207.49	11.94	21.16	3.07	11.83	0.04	1.00	0.99	0.55
55–92	203.88	156.70	16.83	18.00	3.88	8.47	0.38	1.27	1.03	0.69
92–150	329.57	292.56	12.18	19.15	2.91	2.77	5.31	0.98	1.19	0.28
Profile 4										
0–20	160.46	132.77	8.51	16.37	2.81	0.00	0.83	1.08	0.93	1.02
20–40	152.38	126.94	7.13	16.28	2.03	0.00	0.82	1.10	0.80	0.17
40–60	176.97	151.22	7.52	16.46	1.77	0.00	1.11	1.13	0.75	0.15
83–104	198.01	174.46	4.26	17.53	1.76	0.00	0.26	0.81	1.44	0.27
104–150	376.95	327.56	15.03	31.09	3.27	0.00	0.62	0.95	10.03	0.52
Profile 5										
0–20	332.40	268.34	30.01	30.78	3.27	0.00	5.12	2.52	10.00	0.49
20–40	345.20	278.66	25.83	37.72	2.99	0.00	8.91	3.44	15.08	0.31
40–60	332.36	267.01	23.43	37.29	4.63	0.00	5.66	3.21	15.65	1.23
104–110	371.78	298.82	28.97	37.18	6.81	0.00	5.17	1.63	14.50	0.92
110–150	378.49	321.71	13.98	39.29	3.51	0.00	5.33	1.23	15.99	0.56

Table 2 contd.

Profile No.	PWK CEC	Ca^{2+} exch	Mg^{2+} exch	Na^{+} exch	K^{+} exch	H^{+} exch	Ca^{2+} wslb	Mg^{2+} wslb	Na^{+} wslb	K^{+} wslb
	$mmol \cdot kg^{-1}$									
Profile 6										
0–20	298.43	242.00	10.35	41.88	4.20	0.00	0.62	0.99	19.71	1.28
20–40	281.66	213.18	12.35	52.22	3.91	0.00	0.82	1.10	28.38	0.31
40–60	411.53	333.35	13.79	60.10	4.29	0.00	0.90	1.20	31.38	0.46
79–88	316.53	236.60	12.73	62.76	4.44	0.00	8.60	1.58	36.80	0.72
88–108	340.26	260.69	10.30	64.42	4.85	0.00	8.83	1.52	39.80	0.81
108–150	358.34	274.73	10.95	67.95	4.71	0.00	9.43	1.52	42.51	1.21
Profile 7										
0–20	217.43	153.17	10.60	26.75	2.54	24.37	0.68	0.86	1.32	0.21
20–40	237.63	188.90	5.86	20.61	2.13	20.13	0.17	0.66	0.96	0.37
40–60	183.19	139.33	6.81	17.63	2.22	17.20	0.14	0.66	0.80	0.43
84–128	148.32	109.59	6.07	17.76	2.23	12.67	0.07	0.75	0.69	0.95
128–150	132.86	91.42	7.79	17.96	2.72	12.97	0.05	0.87	0.94	0.96

exch – exchangeable, wslb – watersoluble.

In profiles No. 1 and 7 the quantitative predominance of Ca^{2+} cations in horizon of humus accumulation was determined, while in profiles 2, 3, 4 and 5 theses conditions were observed in horizons of parent material. In the research published by Ciesla [4] on not-salt-affected black earths of Kujawy region the content of calcium cations ranged from 61 to 120 $mmol \cdot kg^{-1}$, whereas in soils investigated by Rytelewski et al [5, 6] and Czerwinski [7], effected by sodium industry this concentration was much higher than one hundred $mmol \cdot kg^{-1}$. Sodium was the second cation in soil sorption complex

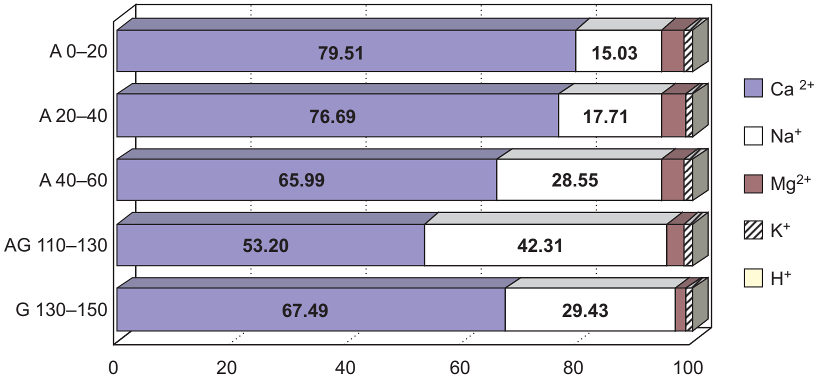

Fig. 2. The percentage of exchangeable cations in the sorption complex of the profile 1

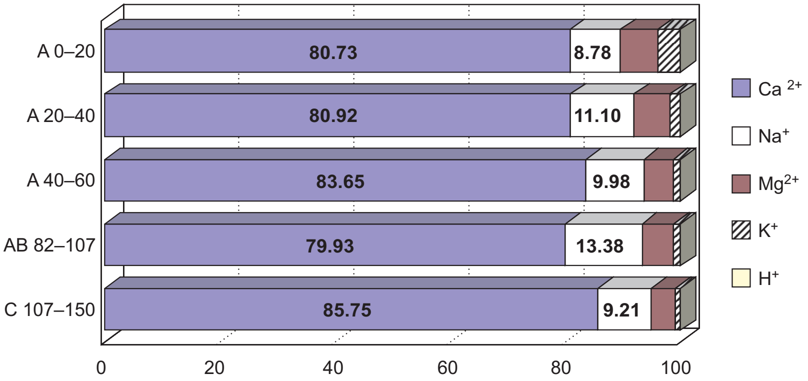

Fig. 3. The percentage of exchangeable cations in the sorption complex of the profile 2

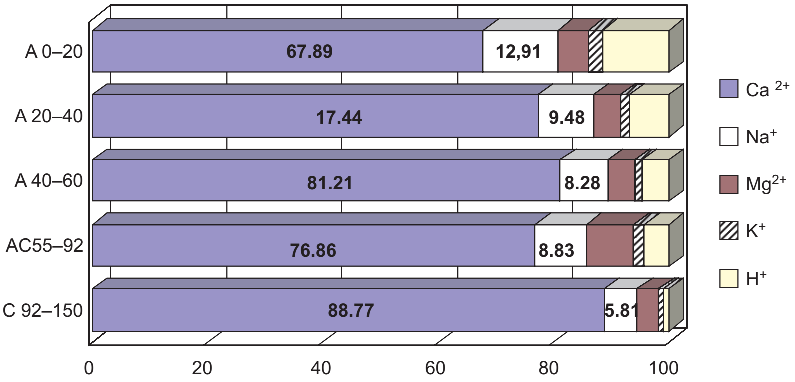

Fig. 4. The percentage of exchangeable cations in the sorption complex of the profile 3

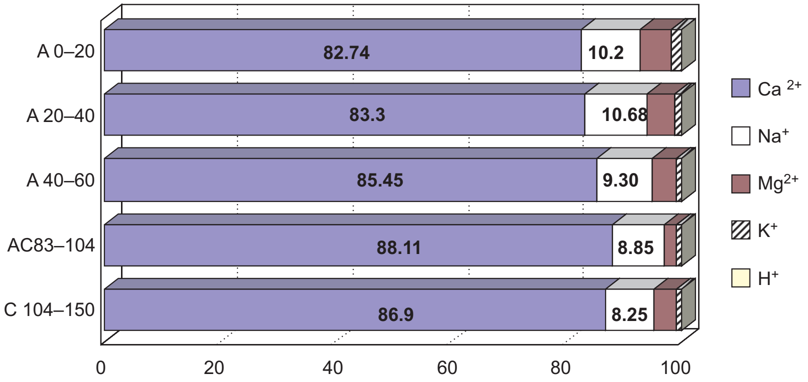

Fig. 5. The percentage of exchangeable cations in the sorption complex of the profile 4

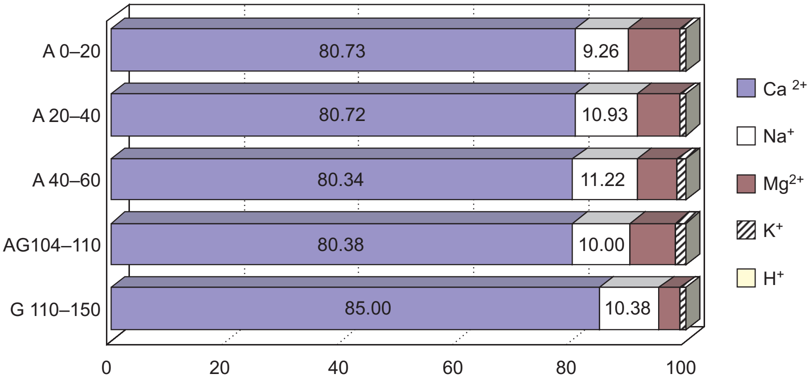

Fig. 6. The percentage of exchangeable cations in the sorption complex of the profile 5

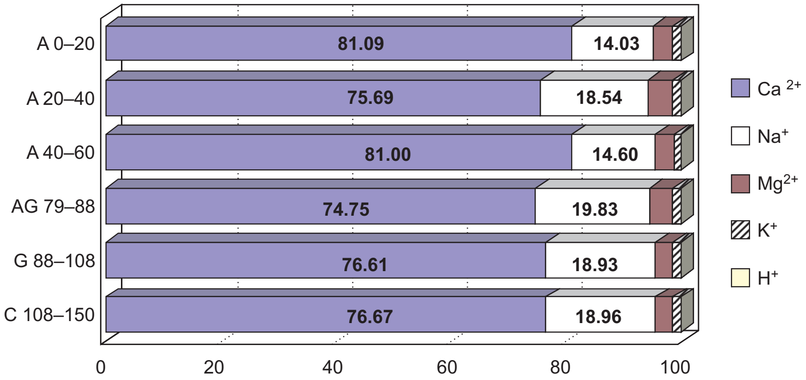

Fig. 7. The percentage of exchangeable cations in the sorption complex of the profile 6

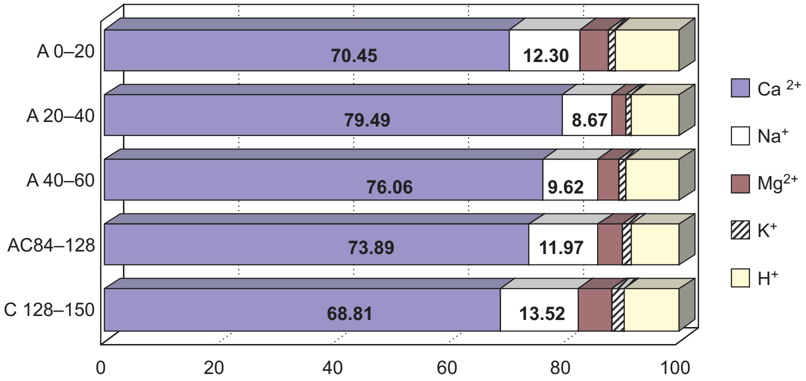

Fig. 8 The percentage of exchangeable cations in the sorption complex of the profile 7

16.28–73.46 mmol · kg^{-1}. In profiles No. 1, 2, 4, 5 and 6 accumulation of these cations was observed in horizons of parent material. In profiles No. 3 and 7 this accumulation was observed in surface horizons (Table 2). Sodium cation as one of the best water soluble cations is wash out with rainfall water into deeper horizons in soil profiles and its high concentration in surface horizons is possible only with continuous inflow of sodium compounds from outer sources (in this case from intensively use of graduation towers especially in the summer) [8]. The detailed research on chemical composition of black earths of Kujawy region conducted by Ciesla [4] in the 1960s confirmed that content of exchangeable sodium cations reached the level of 3–8 mmol · kg^{-1}. The content of Na cations determined in soils contaminated after brine pipeline failure or leakage from settling tank of sodium industry sewage, reached 120–130 mmol · kg^{-1} just after the inflow from contamination source [5, 6, 9]. Soils of investigated area in most horizons were characterized by intermediated values of sodium cations concentration – several times higher than in non-salt-affected black earths and much less than in soils under the influence of sodium industry. The content of exchangeable Mg cations ranged 4.26–30.01 mmol · kg^{-1} (Table 2) and it was the values 4 or 5 times lower than in black earths not under anthropopressure. Potassium exchangeable cations had the smallest content in sorption complex of analysed soils. It was between 1.76–8.15 mmol · kg^{-1} and showed no significant accumulation in any of the soil horizons. The predominance of calcium and sodium cations was confirmed by the results of percentage content of individual cations in sorption complex. In soil profiles No. 1, 2, 4, 5 and 6 analysed cations occurred in following order: Ca^{2+} 53.20–88.11 %; Na^{+} 8.25–42.31 %; Mg^{2+} 1.87–9.03 %; K^{+} 0.81–1.83 % (Fig. 2, 3, 5–7). In profiles No. 3 and 7, with acid reaction these values were as follows: Ca^{2+} 67.89–88.77 %; Na^{+} 5.81–13.52 %; Mg^{2+} 2.47–8.25 %; K^{+} 0.88–2.48 %; H^{+} 0.84–11.40 % (Fig. 4, 8).

The highest concentration in soil solution of the analysed profiles among detected cations were sodium cations 0.69–42.51 mmol · kg^{-1}. Moreover in profiles No. 1, 2, 4, 5 and 6 concentration of water-soluble sodium was increasing due to depth (Table 2). The obtained results of water-soluble Na^{+} were much higher than values for non--salt-affected black earths of Kujawy region, where it averaged at 7 mmol · kg^{-1} [8], but lower than values in soils under the influence of sodium industry reached even 65–100 mmol · kg^{-1} [5]. The concentration of water-soluble calcium cations was on the level between 0.05 mmol · kg^{-1} and 9.43 mmol · kg^{-1}. In soil profile No. 2, 3 and 6 the highest concentration of these cations was observed in horizons of parent material (Table 2). Water-soluble forms of other cations had much lower concentration ranging between 0.66 mmol · kg^{-1} – 3.44 mmol · kg^{-1} for Mg^{2+}, and 0.15 mmol · kg^{-1} – 2.12 mmol · kg^{-1} K^{+}, and did not show any tendency (regularity) in profile distribution of the analysed soils.

Conclusions

1. Dominating element in the sorption complex of the analysed soils, regardless of the soil profile's location, was calcium. Moreover in most endopedons the concentration

of the Ca^{2+} was two or even three times higher than in black earths (Mollic Gleysols) which were not subjected to anthropopression.

2. The soils of the Spa Park in Inowroclaw are black earths of the high content of sodium, which with a little amount of atmospheric precipitation and a constant inflow of sodium from the graduated towers may cause negative changes of their physical properties and composition of a sorption complex. This negative influence of sodium cations may be balanced by a high content of calcium ions.

3. The complex's deficiency in $Mg^{2+}$and K^{+} may be caused by the increased content of Na^{+} in a soil solution and a sorption complex or supplanting, especially magnesium from a complex by calcium ions.

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WPŁYW TĘŻNI NA WARTOŚCI ŚREDNIOROCZNE KATIONÓW W CZARNYCH ZIEMIACH W INOWROCŁAWIU

Katedra Kształtowania i Ochrony Środowiska
Uniwersytet Technologiczno-Przyrodniczy w Bydgoszczy

Abstrakt: Badaniami objęto gleby zlokalizowane w Parku Zdrojowym w Inowrocławiu, będące pod stałym wpływem tężni. Stałe oddziaływanie aerozoli unoszących się z tężni może na tyle zmodyfikować skład chemiczny gleb, że przestaną one w niedalekiej przyszłości funkcjonować jako czarne ziemie, a staną się glebami słono-sodowymi czy glebami antropogennymi słonymi. Ten specyficzny czynnik antropogenny powoduje wzrost stężenia kationów wapniowych i sodowych, zmieniając tym samym istotnie skład kompleksu sorpcyjnego analizowanych gleb. Analizy zawartości poszczególnych kationów w kompleksie sorpcyjnym wykazały wyraźną dominację jonów wapnia (91.42–333.35 mmol $\cdot$ kg^{-1}), który w kilku profilach uzyskał często dwu- lub nawet trzykrotnie wyższe wartości stężenia niż w czarnych ziemiach kujawskich nie poddanych antropopresji. Kolejne miejsce w obsadzie kompleksu sorpcyjnego zajmował sód (16.28–73.46 mmol $\cdot$ kg^{-1}). Badane gleby przyjmowały w większości poziomów wartości pośrednie stężenia sodu wymiennego, to znaczy charakteryzowały się kilkukrotnie większym stężeniem kationów sodowych w stosunku do niezasolonych czarnych ziem, jednak mniejszymi wartościami stężenia Na^+ niż w glebach poddanych silnej antropopresji przez przemysł sodowy. Pozostałe analizowane pierwiastki (Mg^{2+}, K^+) charakteryzowały się niskim stężeniem zarówno w kompleksie sorpcyjnym, jak i roztworze glebowym i nie wykazywały cech akumulacji w którymkolwiek z poziomów genetycznych.

Słowa kluczowe: czarne ziemie, właściwości fizykochemiczne, antropopresja, tężnie

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Jacek GRZYB[1] and Krzysztof FRĄCZEK[1]

ACTIVITY OF PHOSPHOHYDROLYTIC ENZYMES IN WATERS

AKTYWNOŚĆ ENZYMÓW FOSFOHYDROLITYCZNYCH W WODACH

Abstract: Phosphorus occurs in mineral and organic forms in aquatic environments. Much of the available phosphorus resources occur in organic forms which are impossible to use directly by living organisms – cytoplasmic membranes of microorganisms' cells transport almost exclusively orthophosphates. Biological decomposition of organic phosphorus combinations is one of the key stages of phosphorus cycle in surface waters. This process is possible due to existence of a group of phosphohydrolytic enzymes, such as: 5'-nucleotidase, endo- and exonucleases, phytase and phosphatases. Occurrence or activity of these enzymes was found in all components of plankton: bacteria, cyanobacteria, algae, fungi, single- and multicellular plankton animals. Activity of phosphohydrolytic enzymes directly affects productivity of aquatic ecosystems.

Keywords: phosphorus, organic matter, activity of enzymes, water

Phosphorus is one of the elements that are strictly necessary for life of all living organisms. Although, in comparison with carbon and nitrogen, aquatic organisms require small amounts of this nutrient for growth and development (for example molar ratio of C:N:P in biomass of algae equals 106 : 16 : 1), its role in a cell is versatile. It is one of a cell building materials, *eg* phospholipids that build cytoplasmic membrane, compounds which store and transfer energy, *eg* ATP, phosphoenolpyruvic acid, many coenzymes or structures that store and express genetic information – DNA and RNA [1, 2].

Phosphorus occurs in mineral and organic compounds (as dissolved organic phosphorus or phosphorus enclosed in molecular matter) in aquatic environments. Fraction of mineral phosphorus is composed mainly of PO_4^{3-}, HPO_4^{2-}, $H_2PO_4^{-}$ ions, various indecomposable orthophosphates or their condensates. Definite majority of organic derivatives of phosphorus consists of various monoesters and diesters of orthophosphoric acid (phosphatides). The compounds that contain P-N binding (phosphocreatine or phosphoarginine) are the only exceptions. Availability of phosphorus resources in Earth hydrosphere is limited. Firstly, phosphorus consisting minerals are

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[1] Department of Microbiology, University of Agriculture in Krakow, al. A. Mickiewicza 24/28, 30–058 Kraków, Poland, email: rrgrzyb@cyf-kr.edu.pl, rrfracze@cyf-kr.edu.pl

weakly soluble and relatively rare, so supply of this element to aquatic environments as an effect of erosion and weathering of rocks is minimal. Secondly, global transport of phosphorus is directed almost one-way. This element moves from land ecosystems to inland waters and finally to seas and oceans, where it is practically immobilised for a long time in sedimentary rocks formed in these ecosystems. Duration of phosphorus in these reservoirs equals on average several thousand years [3].

Currently, many various mineral and organic substances enter aquatic ecosystems as a result of human activity. Among them nitrogen and phosphorus, nutrient sources for organisms living in water, can be found. Apart from metabolites of living organisms, soil erosion and weathering of rocks, also various mineral and organic combinations of phosphorus that do not occur in natural state, *eg* synthetic polyphosphates incorporated in detergents or pesticides occur in the pool of phosphorus containing compounds [4–6].

Common presence of phosphorus in many cell structures and important role of this element in metabolism caused that content and transformations of phosphorus became of particular interest of scientists and main objective of research projects within last few decades. Principal conclusion of these studies was a statement that content of phosphorus and its derivatives is a basic factor that controls biological production and evolution [7–12].

Phosphorus is a major nutrient that affects algae growth in surface waters. Biological decomposition of organic combinations of phosphorus is one of key stages of phosphorus cycle in surface waters, because cytoplasmic membranes of microorganism cells transport almost exclusively orthophosphates (PO_4^{3-}) and small amounts of phosphoglycerol and exceptionally phosphopentoses. The rate of mineral phosphorus release determines $P\text{-}PO_4$ assimilation rate by specified biocenoses. Thus, processes that aim at making phosphorus resources available for growth and development of living organisms are extremely important. Enzymatic decomposition of organic phosphorus carried out by four major groups of phosphohydrolytic enzymes is one of these processes [13].

Microorganisms, particularly heterotrophic bacteria, play crucial role in cycles of elements and organic matter decomposition. Majority of these processes depends on microorganisms abilities to produce ectoenzymes. Phosphohydrolases produced by microorganisms are very important for phosphorus mineralisation and supply of inorganic phosphates. Also large number of labile organic compounds that act as bacterial substrates is formed in a cycle of gradual enzymatic reduction of polymeric organic matter. Proteins, polysaccharides, lipids or nucleic acids belong to this category of polymers. They are a significant fraction of dissolved organic matter which is the most important source of nutrients and is hydrolysed and then used by aquatic micro-heterotrophic organisms [7, 13].

Phosphohydrolases as ectoenzymes

Microorganisms that produce ectoenzymes are probably the most likely to win the competition for inorganic as well as for organic nutrients in aquatic environment. Ectoenzymes transform unavailable components of organic matter into easily adoptive and easily penetrable through cellular membranes substrates for microorganisms, also called UDOM fraction (*ultrafiltered dissolved organic matter*). Because ectoenzymes are located on the cell surface, they make UDOM fraction components easily available for the cell transport system. It increases chance of microorganisms to survive in aquatic environment, where availability of energy and nutrients is a factor that limits growth and proliferation of population. Heterotrophic bacteria associated with organic matter particles are the most effective in ectoenzymes production. Specific activity of some ectoenzymes calculated for bacteria cells may be 2 to 20 times higher for *fraction associated with cells* (ectoenzymes) than for "free" enzymes [14].

Production of ectoenzymes which degrade substrates resistant to decomposition by other microorganisms may give their producers advantage in nutrients availability and let dominate the ecosystem. What is more, ectoenzymes producing bacteria are the significant part of aquatic ecosystem, in which they not only make carbon, phosphorus and nitrogen available for themselves by organic matter decomposition, but also influence count of algae by supplying them with nutrients [15].

Four major groups of phosphohydrolytic enzymes produced by aquatic organisms take part in processes of decomposition of organic compounds of phosphorus: 5'-nucleotidase, endo- and exonucleases, phytase and phosphatases. Occurrence or activity of these enzymes was found in all components of plankton: bacteria, cyanobacteria, algae, fungi and single- and multicellular plankton animals [16–19].

The majority of above-mentioned enzymes are functionally ectoenzymes. Only some of them occur in water as free enzymes or enzymes adsorbed on seston particles or on mineral particles and particles associated with biofilm "matrix". Ectophosphohydrolases of eukaryotic microorganisms are located on external surfaces of cytoplasmic membrane, in Gram-positive bacteria in cell wall whereas in Gram-negative bacteria in periplasmic space or in its boundary structures [20, 21].

Activators and inhibitors of phosphohydrolases

Activity of ectoenzymes in waters mostly depends on environmental factors, such as: temperature, pH, inorganic and organic compounds, UV-B radiation and presence of activators and inhibitors or lack of inhibitors. Divalent metal ions are activators for alkaline phosphatases. Alkaline phosphatase activity is stimulated by magnesium, which binds with active site of every part of enzyme. This site differs from the active site for zinc. Magnesium ion causes allosteric modulation, which stimulates dephosphorylation process. If the site provided for magnesium is bound with zinc cation, with higher affinity than magnesium, it will cause decrease of enzyme activity. Inhibitors of alkaline phosphatase are chelates of bivalent ions, such as EDTA and fluoride ions showing uncompetitive effects. On the other hand, acid phosphatase activity is often inhibited by fluorides. Also in presence of heavy metal ions rapid decrease of phosphatase activity occurs (acid as well as alkaline). Product of phosphatase activity – phosphate ion – is competitive inhibitor, similarly to other multivalent anions of inorganic and organic acids, similar in size and charge distribution to phosphate ion [22–24].

Brief Characteristic of phosphohydrolytic enzymes

5'-nucleotidase is located only in surface structures of bacteria and cyanobacteria. It is more specific than phosphatases, because it can only hydrolyse 5'-mono, di- and triphosphates of nucleotide. This enzyme is used by bacteria, similarly to alkaline phosphatase, to supplement intracellular pool of orthophosphate during deficiency of this compound in environment. Free nucleic acids – DNA and RNA are the most important reservoir of substrates for 5'-nucleotidases in lake waters. They belong to *dissolved organic phosphorus* (DOP) fraction particularly rich in this element, because they contain 9 % of phosphorus, whereas dry mass of algae contains only 2 % P, and dry matter of bacteria – 3 % P [25, 26].

Nucleases take part in pre-hydrolysis of DNA (dDNA) and RNA (dRNA) dissolved in water. Due to methodological reasons it is very difficult to define meaning of nucleic acids, and therefore also meaning of nucleases [27].

Phytase is an adaptive enzyme of bacterial origin, with maximum activity at pH 4–6. Effects of its activity are particularly visible in naturally acid or artificially acidulated waters, where it takes part in releasing phosphates from macromolecular organic phosphorus combinations which are mostly products of decomposition of plant material – from inositol phosphates combined with proteins, lipids and fulvic acid [28].

Phosphomonoesterases also called phosphatases are the most common and usually most active phosphohydrolytic enzymes in water. These enzymes catalyse reactions of splitting phosphate rest from proteins, fats, nucleotides and other compounds. Bacterial phosphatases are intracellular enzymes or they are secreted into environment. It depends on construction of external cellular structures, because Gram-negative bacteria with multilayer cell wall secrete small amount of periplasmic enzymes, whereas Gram-positive bacteria secrete more extracellular enzymes due to lack of one or a few layers of cell wall [23, 29].

Research on *Pseudomonas* bacteria showed [30] that phosphatases are located in periplasmic space. Touati et al [31] described acid phosphatase located in periplasm, produced by *Escherichia coli* (Gram-negative bacteria) in alkaline environments. Extracellular secretion of phosphatases from living cells was found by Glew and Heath [32] from *Micrococcus* (Gram-positive bacteria) and Kobori and Taga [33] from *Pseudomonas* (Gram-negative bacteria). Kobori et al [34] proved presence of constitutive high activity phosphatases in bacteria occurring in coastal waters. Cotner and Wetzel [35] found presence of *Acinetobacter* bacteria in pelagic zone of Third Sister Lake. This organism produces adaptive alkaline phosphatase; activity of this phosphatase increased even a thousand times under conditions of severe shortage of orthophosphate. If high concentration of orthophosphates is found in waters (higher than 140 μgPO_4^{3-} dm^{-3}), then pelagic bacteria produce alkaline phosphatase, which activity is inhibited by shortage of organic carbon rather than by phosphorus [36].

Phosphatases are also synthesised by most algae species. In algae they are located on the cell surface, in cellular membrane or secreted outside the cell [37–39].

There is also a part of the fraction of enzymes called "free" enzymes. This fraction consists of dissolved enzymes actively secreted by living algae cells, zooplankton and bacteria; they constitute an important part of total phosphatase activity. Part of activity of this fraction also comes from leakage of contents of aging cells or due to their damage by herbivorous organisms, decomposition of dead cells, their fragmentation, autolysis or lysis of living algae cells by bacteria or non-bacteria parasites. Free enzymes, unlike ectoenzymes do not have contact with cellular structures as a result of physico-chemical processes or after lysis of cells that produce them. Usually their activity, in comparison with the one observed in ectoenzymes is small and is usually a few percent high. Alkaline phosphatase, which connection with cytoplasmic membranes is often weak, may be an ectoenzyme as well as a free enzyme. In turn, 5'-nucleotidase does not occur in environment in "free" state [20, 40, 41].

Resume

Aquatic microorganisms produce a range of hydrolytic enzymes. Activity of this enzymatic potential, particularly bacterial but also algal, influences rate of organic matter assimilation in aquatic environments, which directly influences productivity of ecosystems [42]. Heterotrophic activity of multi-species bacteriocenoses is an indicator that well reflects degree of intensity of organic matter transformation processes in natural ecosystems [43].

Conclusions

1. Availability of phosphorus in aquatic environments is limited, therefore processes that aim at making it available for aquatic microorganisms are crucial.
2. Organic phosphorus decomposition is carried out by four groups of phosphohydrolytic enzymes: 5'-nucleotidase, endo- and exonucleases, phytase and phosphatases.
3. Activity of phosphohydrolytic enzymes was found in all components of plankton: bacteria, cyanobacteria, algae, fungi, single- and multicellular plankton animals.
4. Activity of phosphohydrolytic enzymes in waters is affected by the following environmental conditions: temperature, pH, inorganic and organic compounds, UV-B radiation and presence or lack of activators and inhibitors or lack of inhibitors.
5. Activity of phosphohydrolytic enzymes determines rate of organic matter assimilation in aquatic environments, which directly influences productivity of ecosystems.

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AKTYWNOŚĆ ENZYMÓW FOSFOHYDROLITYCZNYCH W WODACH

Katedra Mikrobiologii
Uniwersytet Rolniczy im. Hugona Kołłątaja w Krakowie

Abstrakt: W środowiskach wodnych fosfor występuje w postaci związków mineralnych i organicznych. Znaczna część dostępnych zasobów fosforu ma postać organiczną, niemożliwą do wykorzystania przez organizmy żywe bezpośrednio. Przez błony cytoplazmatyczne komórek mikroorganizmów są transportowane prawie wyłącznie jony ortofosforanowe. Biologiczny rozkład organicznych połączeń fosforu jest jednym z kluczowych etapów obiegu fosforu w wodach powierzchniowych. Jest to możliwe dzięki grupie enzymów fosfohydrolitycznych, takich jak: 5'-nukleotydaza, endo- i egzonukleazy, fitaza oraz fosfatazy. Występowanie lub aktywność tych enzymów stwierdzono we wszystkich składnikach planktonu: bakteriach, sinicach, glonach, grzybach oraz jedno- i wielokomórkowych zwierzętach planktonowych. Aktywność enzymów fosfohydrolitycznych wpływa bezpośrednio na produktywność ekosystemów wodnych.

Słowa kluczowe: fosfor, materia organiczna, aktywność enzymów, woda

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Małgorzata RAFAŁOWSKA[1]
and Katarzyna SOBCZYŃSKA-WÓJCIK[1]

EFFECT OF AGRICULTURAL PRODUCTION ON ORGANIC MATTER ACCUMULATION IN THE BOTTOM DEPOSITS OF PILWA BAY (LAKE DOBSKIE)

WPŁYW PRODUKCJI ROLNEJ NA AKUMULACJĘ MATERII W OSADACH DENNYCH ZATOKI PILWA (JEZIORO DOBSKIE)

Abstract: This study examined selected physical and chemical parameters of bottom deposits in the Pilwa Bay (Lake Dobskie) supplied by watercourses draining intensively farmed areas. The chemical composition of bottom deposits was analyzed in 2007. It was found that long-term exposure to agricultural pollution and vegetation growth in the Bay contributed to the deposition of bottom sediments. The accumulation of biogenic elements in the surface layer of bottom deposits reached 77.0 kgN_{tot}, 11.0 kgP_{tot}, 8.0 kgK, 704 kgCa, 59.6 kgMg, 17.1 kgNa per hectare of catchment area, and it was equivalent to 14-year nitrogen loads, 36-year phosphorus loads, 2-year potassium loads, 8-year calcium loads, 5-year magnesium loads and 2-year sodium loads. The accumulation of biogenic elements in the bottom deposits of Pilwa Bay plays a key role in protecting the lake's environment against pollution under natural conditions. With respect to their accumulation in bottom deposits, the analyzed elements may be arranged in the following descending order: $Ca > N_{tot} > Mg > Na > P_{tot} > K$.

Keywords: bottom deposits, biogenic elements, Pilwa Bay

Introduction

Mineral and organic material of allochthonous and autochthonous origin is deposited at the bottom of water bodies, composed of various rock formations. Similarly to soils on land, bottom deposits are a combination of crystalline and amorphous minerals with a different grain size and a varied content of organic matter as well as colloidal mineral and organic substances [1].

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[1] Department of Land Improvement and Environmental Management, University of Warmia and Mazury in Olsztyn, pl. Łódzki 2, 10–957 Olsztyn, Poland, phone: +48 89 523 39 92, email: malgorzata.rafalowska@uwm.edu.pl

Bottom deposits are an integral component of the aquatic environment. They play an important role in the biogeochemical cycle, they are the place of deposition and chemical transformation of various compounds supplied to water bodies, and they are the habitat of aquatic organisms [2, 3]. The impact of bottom deposits on the water environment grows with an increase in the accumulated nutrients' availability for aquatic organisms [4]. The chemical composition of deposits is a reliable indicator of surface water purity, and chemical analyses support the determination of changes in heavy metal concentrations in the aquatic environment, even if surface waters are marked by relatively low heavy metal levels [5].

In agricultural catchments, the composition of bottom deposits is determined mostly by the type of land use in a lake's catchment area. Pollutants supplied with surface runoffs from farmland may lead to changes in the composition of bottom deposits.

The objective of this study was to evaluate the effect of intensively farmed areas on the accumulation of bottom deposits in the Pilwa Bay, their differentiation in the horizontal profile and the volume of the accumulated organic matter and biogenic elements.

Materials and methods

The analyzed bottom deposits were sampled in the Pilwa Bay, Lake Dobskie, in the mesoregion comprising the Land of Great Masurian Lakes, Gizycko district. Lake Dobskie constitutes the western part of the Mamry Lake complex, and it has the features of a typical basal moraine lake. The lake occupies a total area of more than 17 km^2. The bay has an area of 52.98 ha, with an average depth of 1.36 m and a well-developed shoreline (k = 1.88). The present bay is a remnant of a former section of Lake Dobskie spanning an area of 100 ha. The western part of Pilwa Bay is supplied by inflows from the lake's catchment comprising semi-intensively farmed areas with an intensive fertilization regime. Selected parts of Lake Dobskie's catchment receive high nitrogen loads from farm fields. The morphometric features of the bay are presented in Table 1.

Table 1

Morphometric parameters of Pilwa Bay

Parameter	Value
Water table surface area [ha]	52.98
Maximum depth [m]	3.66
Average depth [m]	1.36
Volume [m^3]	719288
Maximum length [m]	1733
Maximum width [m]	400
Shoreline length [m]	4847
Shoreline development	1.88
Latitude	54°05′40″
Longitude	21°35′5″

Samples were collected using the ELCMAN sampling kit. In view of the bay's bathymetric features, shape and the varied physical and chemical composition of bottom deposits, the Pilwa Bay was divided into three parts according to the direction of outflows: the western, central and eastern part connected with the main basin of Lake Dobskie. Deposit samples were collected according to the experimental design shown in Fig. 1.

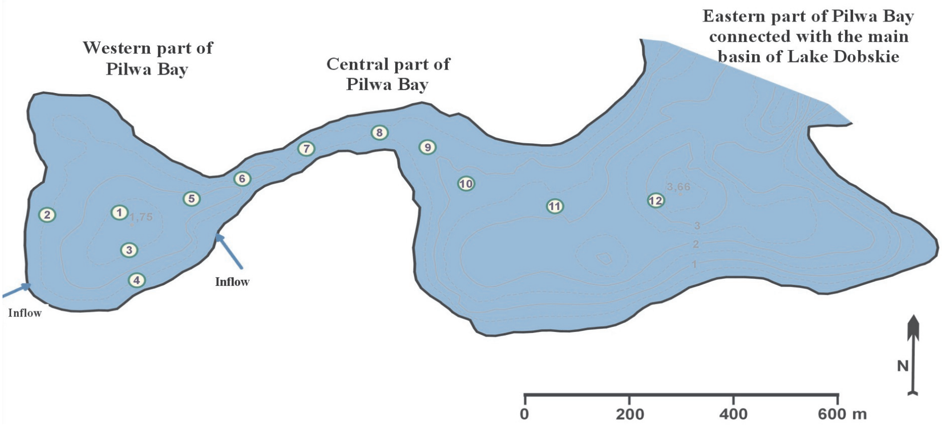

Fig. 1. Bottom deposit sampling sites in Pilwa Bay

Deposit samples were subjected to chemical analyses in the District Analytical and Agricultural Station in Olsztyn, according to Polish Standard PN 88/R-04013. The samples were mineralized in sulfuric acid to determine the content of: total nitrogen (N_{tot}) – by potentiometric titration with sodium bromide, total phosphorus (P_{tot}) – by colorimetry, potassium (K), calcium (Ca), sodium (Na) and magnesium (Mg) – by flame photometry, dry residue – by the gravimetric method (105 ^{o}C), residue after ignition – by the gravimetric method (550 ^{o}C), and pH was determined in a KCl solution.

The Pearson's correlation coefficient was calculated at a significance level of $\alpha = 0.05$ to determine the correlations between the studied parameters.

Results and discussion

The reaction of the investigated bottom deposits was determined in the range of pH_{KCl} 7.15 to pH_{KCl} 7.18, and the average for the entire bay reached pH_{KCl} 7.16 (Table 2).

The average volume density of deposits was leveled throughout the investigated area (1.15 g · cm^{-3}). The studied deposits were characterized by a high degree of hydration and low consolidation. Owing to the bay's relatively small depth, deposits are easily lifted from the bottom, and they are left floating in the water. A high water content of the sampled deposits (86.96 to 89.02 %) indicates that the processes of resuspension and exchange of deposit – water components take place in the examined layer. The least hydrated deposits were found in the central part of the bay where dry matter content reached 13.04 %. In this part of the bay, the collected deposits were marked by a higher content of mineral fractions, as demonstrated by the ash to organic matter ratio of 78.07 % : 21.94 % (Table 2). The highest organic matter concentrations were noted in the eastern part of the bay (40.17 %) characterized by the greatest depth (3.66 m), and the lowest – in its central part (21.94 %). According to Golebiowski and Trojanowski et al [6, 7], deposits sampled at greatest depths are usually marked by the highest accumulation of organic matter. The results of this study support the above findings.

Table 2

Physical properties of the surface layer of bottom deposits in Pilwa Bay

Parameter	Unit	Sampling site			
		Western part of Pilwa Bay	Central part of Pilwa Bay	Eastern part of Pilwa Bay connected with the main basin of Lake Dobskie	Mean
Dry matter	%	10.98	13.04	11.92	11.98
Volume density	$g \cdot cm^{-3}$	1.15	1.15	1.16	1.15
Reaction	pH_{KCl}	7.18	7.15	7.17	7.16
Ash (reside after ignition)	% d.m.	71.98	78.07	59.83	69.96
Organic matter	% d.m.	28.02	21.94	40.17	30.04

Nutrient concentrations varied in the sampled deposits. In the analyzed group of elements, calcium had the highest share with an average of 106.75 $gCa \cdot kg^{-1}$ d.m. for the bay area (Table 3). Calcium concentrations in the analyzed deposit samples ranged from 93.48 to 115.50 $gCa \cdot kg^{-1}$ d.m. According to Januszkiewicz [8], calcium is found in bottom deposits mostly in the form of calcium carbonate. Similarly to other elements, it may be supplied to the water body from the catchment area, mainly during the spring high water stage. Autochthonous matter is yet another source of calcium in bottom deposits.

The studied deposits contained also substantial quantities of nitrogen. The highest amounts of this element were determined in samples from the central part of the bay at 13.28 $gN_{tot} \cdot kg^{-1}$ d.m. on average. The above results suggest that nitrogen is accumulated in this part of the bay, and these findings constitute valuable data for designing protection schemes for the examined lake. The central part of the bay is characterized by the smallest depth and high trophy levels. Mineral deposits feature a powerful system of thick roots which uplift the bottom. The spatterdock had a 50 % to 75 % share of local vegetation rooted in the bottom with leaves floating on the surface. The shallow central part of the bay (depth of around 1 m) contributes to the decomposition of organic matter due to greater exposure to light and higher temperatures. Fertile deposits also support rush growth. The quantities of nitrogen in deposits accumulated nearer the inflows were around two-fold higher than in more distant locations. In this part of the bay, the main source of nitrogen were pollutants and surface runoffs from intensively farmed areas (fertilized with animal slurry). Deposits sampled in the eastern part of the bay were also characterized by higher nitrogen concentrations (Table 3). As noted by Szyperek and Skonieczek [9, 10], the above could result from the fact that nitrogen supplied via surface runoffs migrates to deeper locations where it is accumulated.

The analyzed deposit samples contained significantly lower levels of total phosphorus in comparison with nitrogen. Phosphorus concentrations were also marked by a lower degree of variation (from 1.50 to 2.04 $g \cdot kg^{-1}$ d.m.). Phosphorus levels decreased as the distance from the inflow increased. Similarly to nitrogen, phosphorus was supplied from the catchment, and the above contributed to the accumulation of biogenic elements in bottom deposits. In comparison with calcium and nitrogen, the relatively low phosphorus concentrations in deposits could have resulted from the recirculation of the studied element. Despite a high degree of sedimentation, phosphorus is quickly replenished in water as a result of the exchange between water and bottom deposits. In an environment conducive to resuspension (wave motion in shallow areas) and under oxygen deficiency, high quantities of phosphorus may be released from deposits, especially during the growing season when the studied element is in high demand for primary production needs [11].

Phosphorus is one of the key factors contributing to eutrophication, and it plays a double role in bottom deposits. The quantity of accumulated phosphorus is indicative of bottom deposits' effectiveness as a mechanism for trapping migrating phosphorus, yet high concentrations of this biogenic element may contribute to shallowing processes in the basin of the water body [12].

Potassium is an element with a variety of agricultural applications, and although it does not contribute to water eutrophication, it can be a good indicator of farming intensity in the catchment area. In the analyzed deposits, potassium concentrations ranged from 1.01 to 1.84 $g \cdot kg^{-1}$ d.m. Similar results (0.66 to 1.31 $g \cdot kg^{-1}$ d.m.) were reported by Szyperek [9] who studied a group of water bodies with both agricultural and afforested catchments. Potassium is actively involved in the life processes of ecosystems, and it weakly migrates in water. Among cations, the highest uptake by plants is reported in respect of this nutrient [13].

The magnesium content of the studied deposit samples was relatively leveled, ranging from 8.11 do 9.46 $g \cdot kg^{-1}$ d.m. Magnesium compounds accumulated in bottom deposits do not originate from soil mineral components, and they are supplied mainly by decomposing plants. A similar trend was noted for sodium. With respect to their accumulation in bottom deposits, the analyzed elements may be arranged in the following descending order: $Ca > N_{tot} > Mg > Na > P_{tot} > K$.

The results of this study indicate that agricultural catchments supply substantial biogenic loads. Excess fertilizer nutrients, of both organic and mineral origin, which are not used in farming are distributed in the environment [14].

The volume of nutrients accumulated in the surface layer of bottom deposits points to high dynamics of matter deposition. The level of accumulation is largely determined by the intensity of nutrient supply and the susceptibility of biogenic substances to

Table 3

The content of biogenic elements, ash and organic matter in the surface layer of bottom deposits in Pilwa Bay [g · kg^{-1} d.m.]

Sampling site	Sample no.	N_{tot}	P_{tot}	K	Ca	Mg	Na	Ash (reside after ignition)	Organic matter
Western part of Pilwa Bay	1	6.33	2.20	1.89	115.50	7.40	3.53	654.6	345.4
	2	12.20	2.20	1.98	110.50	8.59	1.83	644.0	356.0
	3	8.03	1.80	1.97	102.50	10.28	2.59	700.8	299.2
	4	12.30	2.20	1.79	108.32	9.96	1.51	758.5	241.5
	5	6.48	1.80	1.57	110.50	11.05	3.15	841.2	158.8
	Mean	**9.07**	**2.04**	**1.84**	**109.46**	**9.46**	**2.52**	**719.8**	**280.2**
Central part of Pilwa Bay	6	13.53	1.80	1.09	118.00	7.51	0.42	598.0	402.0
	7	13.60	1.40	0.95	102.50	8.67	1.26	890.4	109.8
	8	12.70	2.20	1.09	102.50	8.16	3.12	853.6	146.4
	Mean	**13.28**	**1.80**	**1.05**	**107.67**	**8.11**	**1.60**	**780.7**	**219.4**
Eastern part of Pilwa Bay connected with the main basin of Lake Dobskie	9	16.35	1.40	0.85	93.48	6.48	3.62	818.8	181.2
	10	14.35	1.80	0.98	107.00	9.80	2.57	510.6	489.4
	11	10.33	1.40	1.27	108.00	8.50	3.10	563.8	436.2
	12	8.20	1.40	0.93	104.00	9.90	0.94	500.0	500.0
	Mean	**12.27**	**1.50**	**1.01**	**103.12**	**8.67**	**2.56**	**598.3**	**401.7**

permanent sedimentation. The supplied nutrient loads are mostly affected by the type of land use and farming intensity in agricultural catchments [15, 16]. The volume of deposited nutrients is also affected by their concentrations, the thickness and surface area of bottom deposits. The above parameters varied substantially in the bay and, as a result, the estimated values of macronutrient deposition differed significantly

Table 4

The inflow of biogenic load via watercourses feeding into the Pilwa Bay
and the accumulation of biogenic elements in the surface layers of bottom deposits

Parameter	Inflow via watercourses	Accumulation in bottom deposits		
	$[kg \cdot ha^{-1} \cdot year^{-1}]$	$[kg \cdot water\ body^{-1}]$	$[kg \cdot m^2$ bay surface area]	$[kg \cdot ha^{-1}$ catchment surface area]
Total N	5.4	163 893	0.309	77.0
Total P	0.3	23 423	0.044	11.0
K	4.7	17 467	0.033	8.0
Ca	89.0	1 498 254	2.83	704.0
Mg	11.6	126 903	0.24	59.6
Na	7.1	36 477	0.07	17.1

The following quantities of nutrients were accumulated in the bay's bottom deposits: 163893 kgN_{tot}, 23423 kgP_{tot}, 17467 kgK, 149825 kgCa, 126903 kgMg and 36477 kgNa. In the group of analyzed elements, the highest accumulation values were reported for calcium. Based on a more objective indicator, *ie* accumulation per unit area, the following nutrient quantities were determined per m^2 of the bay's bottom area: 0.309 kgN, 0.044 kgP, 0.033 kgK, 2.83 kgCa, 0.24 kgMg and 0.07 kgNa. As regards biogenic element deposition relative to the surface area of the catchment, the following quantities of the analyzed elements were determined per hectare of catchment area: 77.0 kgN_{tot}, 11.0 kgP_{tot}, 8.0 kgK, 704.0 kgCa, 59.6 kgMg and 17.1 kgNa. The following annual loads were supplied via drains from the catchment to the western part of the bay: $5.4\ kg \cdot ha^{-1}\ N_{tot}$, $0.3\ kg \cdot ha^{-1}\ P_{tot}$, $4.7\ kg \cdot ha^{-1}$ K, $89.0\ kg \cdot ha^{-1}$ Ca, $11.6\ kg \cdot ha^{-1}$ Mg and $7.1\ kg \cdot ha^{-1}$ Na.

The Pearson's correlation coefficient was calculated at a significance level of $\alpha = 0.05$ to determine the correlations between the studied parameters (Table 5). The results of a statistical analysis indicate a highly significant correlation between potassium, sodium and nitrogen at $r = 0.60$, between pH, sodium and ash at $r = -0.70$, and between pH and organic matter at $r = 0.72$. The highest value of the correlation coefficient was noted between ash and organic matter at $r = -1.0$. High but statistically non-significant values of the correlation coefficient were observed between Mg, organic matter and pH at $r = 0.49$, and the coefficient of correlation between Mg and ash reached $r = -0.49$. No significant correlations were determined between the remaining parameters.

Table 5

Coefficients of Pearson's correlation between the studied parameters of bottom deposits in the Pilwa Bay

Parameter	N_{tot}	P_{tot}	K	Mg	Ca	Na	Ash	Organic matter
P_{tot}	–0.35							
K	–0.63*	0.66*						
Ca	–0.34	0.47	0.42					
Mg	–0.35	0.04	0.29	0.07				
Na	–0.18	0.27	0.23	–0.34	–0.28			
Ash	0.12	0.21	0.04	–0.49	–0.08	0.37		
Organic matter	–0.12	–0.21	–0.04	0.49	0.08	–0.37	–1.00*	
pH	–0.14	–0.09	0.18	0.56	0.29	–0.70*	–0.72*	0.72*

* Correlation coefficient significant at $\alpha = 0.05$.

Conclusions

The following conclusions can be formulated based on the results of the study analyzing bottom deposits in the Pilwa Bay, Lake Dobskie:

1. Long-term exposure to agricultural pollution and vegetation growth in the Bay contributed to the deposition of bottom sediments. With respect to their accumulation in bottom deposits, the analyzed elements may be arranged in the following descending order: Ca > N_{tot} > Mg > Na > P_{tot} > K.

2. The following quantities of biogenic elements were determined per m^2 of the bay's bottom area: 0.309 kgN_{tot}, 0.044 kgP_{tot}, 0.033 kgK, 2.83 kgCa, 0.24 kgMg and 0.07 kgNa. The quantities of nitrogen in deposits accumulated nearer the inflows were around two-fold higher than in more distant locations. The deposition levels of the remaining nutrients were leveled throughout the bay.

3. The accumulation of biogenic elements in the surface layer of bottom deposits reached 77.0 kgN_{tot}, 11.0 kgP_{tot}, 8.0 kgK, 704 kgCa, 59.6 kgMg and 17.1 kgNa per hectare of catchment area, and it was equivalent to 2–36-year loads. With respect to their accumulation levels, the elements supplied by the inflow may be arranged in the following order: P_{tot} > N_{tot} > Ca > Mg > Na > K.

4. The accumulation of biogenic elements in the bottom deposits of Pilwa Bay plays a key role in protecting the lake's environment against agricultural pollution under natural conditions.

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WPŁYW PRODUKCJI ROLNEJ NA AKUMULACJĘ MATERII W OSADACH DENNYCH ZATOKI PILWA (JEZIORO DOBSKIE)

Katedra Melioracji i Kształtowania Środowiska
Uniwersytet Warmińsko-Mazurski w Olsztynie

Abstrakt: W pracy przedstawiono wyniki badań osadów dennych w zatoce Pilwa jeziora Dobskiego, do której dopływają cieki odwadniające obszary o intensywnej produkcji w aspekcie oceny wybranych parametrów fizykochemicznych tych osadów. Badania składu chemicznego osadów dennych przeprowadzono w 2007 r. Stwierdzono m.in., że wieloletni dopływ zanieczyszczeń pochodzący z intensywnej produkcji rolnej i rozwój roślinności w zatoce spowodował zakumulowanie dużej ilości osadów dennych. Akumulacja biogenów w wierzchniej warstwie osadów wynosiła: 77,0 kgN_{og}, 11,0 kgP_{og}, 8,0 kgK, 704 kgCa, 59,6 kgMg, 17,1 kgNa na jeden ha zlewni, co równało się z 14-letnim dopływem azotu, 36-letnim fosforu, 2-letnim potasu, 8-letnim wapnia, 5-letnim magnezu oraz 2-letnim dopływem sodu. Akumulacja biogenów w osadach zatoki stanowi główny element ochrony jeziora przed zanieczyszczeniami w warunkach naturalnych. Oznaczone składniki, pod względem stężenia w osadach dennych można uszeregować następująco: $Ca > N_{og} > Mg > Na > P_{og} > K$.

Słowa kluczowe: osady denne, składniki biogenne, Zatoka Pilwa

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Magdalena DZIĘGIELEWSKA[1], Beata MYŚKÓW[2],
Iwona ADAMSKA[1] and Beata CZERNIAWSKA[1]

SEASONAL DYNAMICS OF THE ACTIVITY OF ENTOMOPATHOLOGICAL NEMATODES (STEINERNEMATIDAE AND HETERORHABDITIDAE) IN SELECTED GREENS OF SZCZECIN

SEZONOWA DYNAMIKA AKTYWNOŚCI NICIENI OWADOBÓJCZYCH STEINERNEMATIDAE I HETERORHABDITIDAE W WYBRANYCH ZIELEŃCACH SZCZECINA

Abstract: Seasonal dynamics of the activity of entomopathogenic nematodes belonging to the families Steinernematidae and Heterorhabditidae in four town greens in Szczecin was examined between April and October 2008. The density of nematodes in the soil and the occurrence of potential hosts at individual sites were analysed. Four species of nematodes were isolated from the sites: *Steinernema feltiae*, *S. affine*, *S. bicornutum* and *Heterorhabditis megidis*. *S. feltiae* occurred at the four sites and was the most common species. The greatest density of nematodes ranging from 7 000 ind./m^2 to 50 000 ind./m^2 was observed in the autumn, which may be connected with an increased availability of hosts in the soil. A relationship was observed between the occurrence of *H. megidis* and the presence of *Otiorrhynchus rotundatus* in tree plantings with oaks. The highest density (over 25 000 ind./m^2) of *H. megidis* was recorded in the autumn. Beetles were among insects that dominated at the study sites with the exception of tree plantings with horse chestnut (*Aesculus hippocastanum*) which were parasitised by the leaf miner belonging to moths.

Keywords: entomopathogenic nematodes, Steinernematidae, Heterorhabditidae, occurrence nematodes, seasonal dynamics nematodes, soil, town greens

The activity of entomopathogenic nematodes (Steinernematidae, Heterorhabditidae) may be limited by a variety of biotic and abiotic factors. However, suitable hosts must be present for parasitic populations of nematodes to survive in the soil. Infective larvae

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[1] Department of Plant Protection, West-Pomeranian University of Technology in Szczecin, ul. J. Słowackiego 17, 71–434 Szczecin, Poland, phone: +48 91 449 63 74, email: entomology@zut.edu.pl

[2] Department of Plant Genetics, Breeding and Biotechnology, West-Pomeranian University of Technology in Szczecin, ul. J. Słowackiego 17, 71–434 Szczecin, Poland, email: bmyskow@zut.edu.pl

of entomopathogenic nematodes use the resources stored in the fat bodies in unfavourable environmental conditions, thus protecting themselves from starvation.

A low species diversity of insects is observed in urban green areas. As anthropopressure increases, the frequency of the soil fauna decreases. Impoverishment of the fauna upsets the circulation of the matter in ecosystems and contributes to an increase in the frequency of phytophages.

Studies on the seasonal biological activity of entomopathogenic nematodes were conducted in selected town greens in Szczecin. Changes in the frequency of parasitic populations of nematodes depending on the observation date were recorded.

Material and methods

Field studies were conducted between April and October 2008 in four selected town greens in Szczecin in which a mass occurrence of phytophagous insects that come into contact with soil during their developmental cycle was observed. The selected greens have linear plantings that form either a hedge (M3) or a set of tree rows. A detailed description of the sites is given in Table 1.

Table 1

Description of sites for research

Sign of site	Place of soil sample	Distance of a site from the road [m]	Type of green area	Dominant of foliophage insect	Wintering stage of insect
M3	Moniuszki street, Jasne Błonia, Park Kasprowicza	0.5	hedge with the common privet *Ligustrum vulgare*	*Otiorrhynchus rotundatus*, *Coleoptera*	larvae and imago in the soil
M5	Park Kownasa 1 (left site)	50	walking alley with sessile oak *Quercus sessilis* and common oak *Quercus robur*	*Curculio glandium*, *Coleoptera*	larvae and imago in the soil
M6	Park Kownasa 2 (right site)	50	walking alley with sessile oak *Quercus sessilis* and common oak *Quercus robur*	*Curculio glandium*, *Coleoptera*	larvae and imago in the soil
M8	Wojska Polskiego street	0.5	walking alley with the white horse chestnut *Aesculus hippocastanum* along tram	*Cameraria ohridella*, *Lepidoptera*	pupa in deciduous leaves or in the soil

Soil (ca 600 cm^3) was sampled from a depth of 20–30 cm at monthly intervals. Entomological nematodes were isolated from the soil with the baiting method using *Galleria mellonella* [1, 2]. Containers with the soil and insects (six containers for each soil sample, three insects in each container) were incubated at 22–24 ^{o}C. Dead insects were selected to estimate the number of mature nematodes inside the host's body. The number of all nematodes recorded in the insects from a single soil sample was added up and the density of nematodes per 1 m^2 was calculated (ind./m^2). Nematodes isolated from the soil were determined to the species level using morphological and morphometric characters of male insects and infective larvae (J_3).

Results

Four nematodes: *Steinernema feltiae*, *S. affine*, *S. bicornutum* and *Heterorhabditis megidis* were isolated from the soil collected from four town greens. The greatest species diversity was observed in the town green with wild privet (*Lugustrum vulgare*) (M3) where *Otiorrhynchus rotundatus* (lilac weevil) dominated and with tree plantings with oaks where *Curculio glandium* (acorn weevil) occurred (M5, M6), (Table 1, Fig. 1–3). The occurrence of three out of four nematode species was recorded at these sites (Fig. 1–3). The lowest diversity of nematode species was observed in a narrow set of two rows of trees with horse chestnut that separated transport routes with a high traffic rate (Fig. 4). Only *S. feltiae* was recorded at the site.

The density of nematodes in the soil changed depending on the date and the soil sampling site, and was not continuous. The highest density of the parasites ranging from 7000 ind./m^2 (Fig. 1) to 50 000 ind./m^2 (Fig. 2) was recorded at the sites in October (Fig. 1–4). The mean density of nematodes in the soil at individual sites varied and

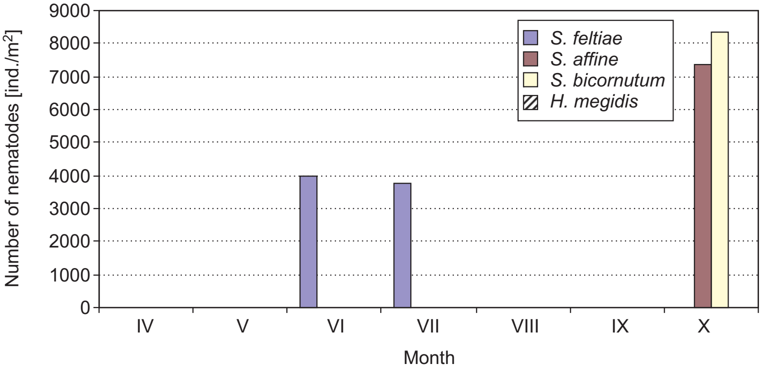

Fig. 1. The trend of numbers of individual entomopathogenic nematodes (Steinernematidae, Heterorhabditidae) in the soil on the M3 site during the season (from April to October 2008)

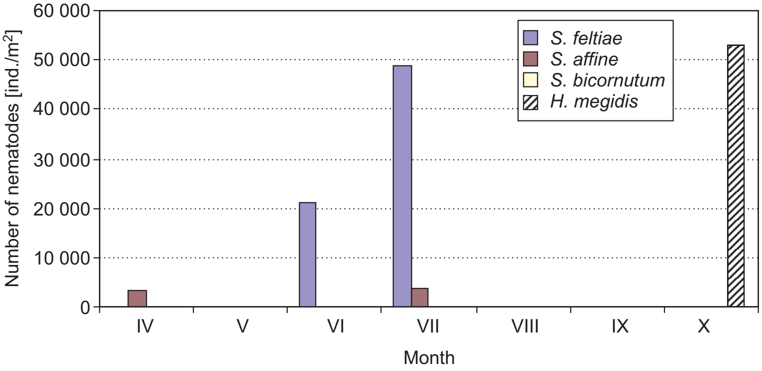

Fig. 2. The trend of numbers of individual entomopathogenic nematodes (Steinernematidae, Heterorhabditidae) in the soil on the M5 site during the season (from April to October 2008)

ranged from 6000 ind./m^2 in the town green with wild privet (site M3) and *ca* 9000 ind./m^2 in the oak alley (site M6) to ca 25 000 ind./m^2 in plantings with horse chestnut (site M8) and oaks (site M5).

Observations show that the occurrence of *Heterorhabditis megidis* nematodes was strictly related to the feeding environment of *Curculio glandium* beetles whose imago winters in the soil (sites M5 and M6) (Fig. 2 and 3). A high density and the domination of the species were recorded in the autumn during an intensified contact between larvae of *Curculio glandium* and the substrate when damaged acorns fell from the trees onto the soil.

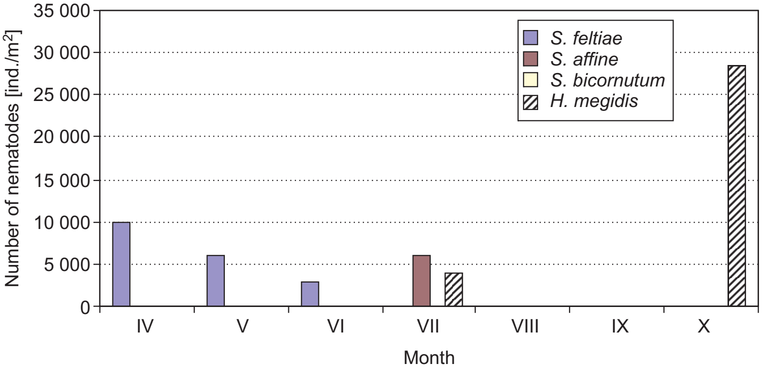

Fig. 3. The trend of numbers of individual entomopathogenic nematodes (Steinernematidae, Heterorhabditidae) in the soil on the M6 site during the season (from April to October 2008)

Steinernema feltiae commonly occurred at all of the sites. It was recorded most frequently in the greens during the spring and summer activity of insects (Fig. 1–3). Observations show that the species has a broad range of hosts and is not strictly related to a specific environment. However, it was the only species that occurred together with the leaf miner at the site with horse chestnut (M8) (Fig. 4). It was recorded in April and

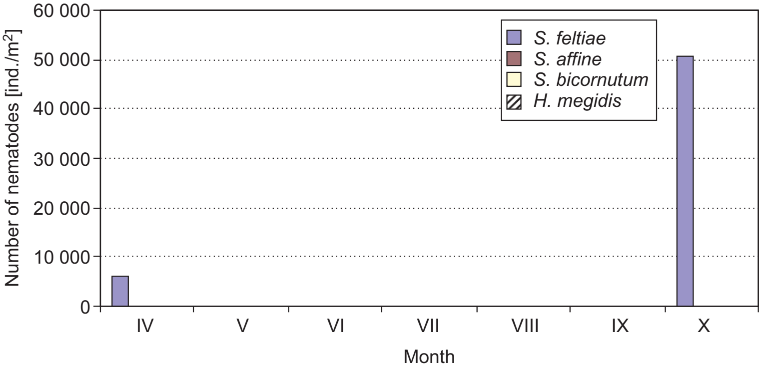

Fig. 4. The trend of numbers of individual entomopathogenic nematodes (Steinernematidae, Heterorhabditidae) in the soil on the M8 site during the season (from April to October 2008)

a high density of *S. feltiae* (50 000/m^2) was observed in October during an increased availability of pupae of the leaf miner in the soil (Fig. 4).

Steinernema affine nematodes were isolated from the majority of the sites. However, their density in the soil remained at a low level that did not exceed 8 000 individuals per m^2. The species often co-occurred with other nematodes: *S. bicornutum* (Fig. 1), *S. feltiae* (Fig. 2) and *H. megidis* (Fig. 3).

S. bicornutum was the least frequently recorded species. It occurred in October at only one site (with wild privet) where beetles of the family Curculionidae, *Otiorrhynchus rotundatus*, dominated.

Discussion

The life cycle of parasitic nematodes belonging to the family Steinernematidae and Heterorhabditidae is strictly correlated with the host development. A high density of nematodes in the soil is a response to insect gradations in the environment [3]. In practice, however, the parasites encounter a natural resistance of the environment that restricts their activity [4–7].

Entomopathological nematodes (Steinernematidae, Heterorhabditidae) commonly occur in the soil. Individual species, however, exhibit different environmental preferences [8, 9]. For instance, *Steinernema kraussei* is mostly associated with tree plantings while *Steinernema feltiae* and *S. affine* are associated with open areas.

Observations show that *S. feltiae*, the most frequently recorded species in Polish soils [6, 11], is very well adapted to diverse environmental conditions and probably has a broad range of hosts. The activity of entomopathogenic nematodes in the soil fluctuated seasonally and was not continuous. Changes in the population density depended on the date and the soil sampling site as well as on food availability. A clear increase in the population density at all the sites was observed in the autumn when insects move into the soil to winter there. It is noteworthy that the greens were characterised by a poor species differentiation of phytophages where one insect species usually dominated and the potential nutritional base mostly consisted of single hosts. In the Czech Republic, a high density of entomopathogenic nematodes was recorded only in the spring at the beginning of the season, followed by a drop in the parasites' density which later remained at a steady level until the end of the season [10]. The occurrence of the host in the soil was considered to be the most important factor conditioning the seasonal activity of nematodes at the study site. This is confirmed by the present observations conducted in town greens where a high density of *Heterorhabditis megidis* in tree plantings with English oak (*Quercus robur*) and sessile oak (*Quercus petraea*) (sites M5, M6) was probably associated with the presence of *Curculio glandium* beetles whose imago winters in the soil and larvae fall on the soil with damaged acorns, enabling contact between entomopathogenic nematodes and potential hosts.

The species composition of entomopathogenic nematodes in town greens is relatively rich [11]. The greatest species diversity of nematodes (three species out of four) was observed in the green with wild privet where *Otiorrhynchus rotundatus* (Coleoptera) fed intensively and in tree plantings with oaks in which *Curculio glandium* (Coleoptera) occurred.

The lowest species diversity was recorded in a narrow set of two tree rows with horse chestnut that separated transport routes with a high intensity rate of traffic. Only *Steinernema feltiae* was recorded at the site. As generally observed, nematodes of the family Steinernematidae dominate in the temperate climate zone while thermophilic nematodes belonging to the family Heterorhabditidae occur less frequently [8–12]. To sum up, ecological relationships of entomopathogenic nematodes can be analysed using examinations of their seasonal activity.

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SEZONOWA DYNAMIKA AKTYWNOŚCI NICIENI OWADOBÓJCZYCH STEINERNEMATIDAE I HETERORHABDITIDAE W WYBRANYCH ZIELEŃCACH SZCZECINA

[1] Zakład Ochrony Roślin, [2] Zakład Genetyki, Wydział Kształtowania Środowiska i Rolnictwa
Zachodniopomorski Uniwersytet Technologiczny w Szczecinie

Abstrakt: Sezonową dynamikę aktywności nicieni owadobójczych z rodziny Steinernematidae i Heterorhabditidae badano od kwietnia do października 2008 r. w czterech zieleńcach Szczecina. Analizowano zagęszczenie nicieni w glebie oraz występowanie potencjalnych żywicieli na poszczególnych stanowiskach. Z badanych stanowisk wyizolowano cztery gatunki nicieni: *Steinernema feltiae*, *S. affine*, *S. bicornutum* i *Heterorhabditis megidis*. Najpospolitszym gatunkiem okazał się *S. feltiae*, który wystąpił we wszystkich zieleńcach. Najwyższe zagęszczenie nicieni zanotowano jesienią od 7 000 os./m^2 do 50 000 os./m^2, co może mieć związek ze zwiększoną dostępnością żywiciela w glebie. Stwierdzono wyraźny związek między występowaniem nicieni *H. megidis* i obecnością słonika żołędziowca w zadrzewieniach z dębem. Najwyższe zagęszczenie (ponad 25 000 os./m^2) tego nicienia zanotowano jesienią. Wśród owadów, które dominowały w badanych środowiskach, były chrząszcze, z wyjątkiem zadrzewień z kasztanowcem białym, gdzie żerował szrotówek kasztanowcowiaczek należący do motyli.

Słowa kluczowe: nicienie owadobójcze, *Steinernematidae, Heterorhabditidae*, występowanie nicieni, sezonowa dynamika nicieni, gleba, zieleńce miejskie

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Zbigniew GORZKA[1], Marcin ZABOROWSKI[1],
Marek KAŹMIERCZAK[1], Andrzej ŻARCZYŃSKI*[1],
Tadeusz PARYJCZAK[1], Adam KĘDZIORA[1],
Radosław CIESIELSKI[1] and Monika PISAREK[1]

DETERMINATION OF AMMONIA AND OTHER POLLUTANTS IN AIR AND IN THE AREA OF POULTRY AND MILKER COWS KEEPING FARMS

OZNACZANIE AMONIAKU I INNYCH ZANIECZYSZCZEŃ W POWIETRZU NA TERENIE FERM HODOWLI DROBIU I KRÓW MLECZNYCH

Abstract: Polluted air in a big farm of poultry keeping (~18 thousands of chickens) and milker cows (30 animals) in Lodz province was sampled. The aim of the investigation was to determine odour pollutants, especially ammonia, in air and check the possibility of a catalytic method application in their removal. Gas samples were analyzed on the spot of sampling with an application of gases analyser Madur GA-20, as well as in a laboratory with an application of instrumental and spectrophotometric methods. The intensity of odours was estimated using five-stage scale applied by local authorities in Japan for odorous protection of air quality. Within sampling period, poultry keeping in the farm was the source of variable in time ammonia emission ranging from 0.82 to 2.65 mg/m^3. Air inside the farm contained carbon dioxide (0–0.3 %) and oxygen (20.5–20.9 %). Carbon monoxide, sulphur dioxide, hydrogen sulphide (> 2.0 mg/m^3) and formaldehyde (> 0.25 mg/m^3) was not detected. The highest odour intensity inside the building of chicken keeping and at outlets of ventilators was at the third stage in odour scale applied in Japan (3.5), *ie*, clearly perceptible. However, it decreased significantly with the increase in a distance from the building. Higher ammonia concentrations were determined inside a cowhouse with milker cattle. They ranged from 3.2 to 5.6 mg/m^3. Ammonia temporary concentration determined during removal of manure was higher and totalled 15.5 mg/m^3. Its highest value (18.8 mg/m^3) was determined in gases above slurry in the septic tank.

Keywords: chicken farms, ammonia determination, cowhouse, odours in agricultural production

Ammonia is a gas toxic not only for animals but also for people, and with negative effect on the natural environment. A global emission of ammonia is estimated at 62 mln Mg (ton) per year and 42 % of this amount originates from an animal farming [1]. In

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[1] Institute of General and Ecological Chemistry, Technical University of Lodz, ul. S. Żeromskiego 116, 90–924 Łódź, Poland, phone: +48 42 631 31 18, fax: +48 42 631 31 28, email: andrzejzarcz@o2.pl

* Corresponding author.

European countries, total emission is estimated at 8 mln Mg (ton) per year and 72 % of this amount comes from an animal farming [2]. In Poland, ammonia emission from agricultural sources was estimated at 314.610 Mg in 2005, according to National Emission Center. 70 % of this emission is ascribed to animal farming (Table 1) [1].

Table 1

Ammonia emission from the agriculture in Poland in 2005 [1]

Emission sources	Emission indicator	Unit	Emission [Mg (ton)]
Agriculture total			314.610
Cultivation with fertilizers application	9.8	%	87.740
Milker cows	27.8	kg per animal	76.580
Residual cattle	12.5	kg per animal	32.880
Fattening pigs	5.1	kg per animal	95.430
Sheep	1.9	kg per animal	0.600
Horses	12.5	kg per animal	3.900
Hens	0.32	kg per animal	14.460
Residual poultry	0.26	kg per animal	3.010

Poultry keeping as well as cattle keeping farms, are the biggest sources emitting pollutants of all types, *ie* chemical – gases, mechanical – dusts and biological – microorganisms. Ammonia is the most noxious gas for the environment, produced by poultry keeping farms. Ammonia is generated in poultry houses as a by-product during microbiological decomposition of organic compounds containing nitrogen in droppings and residual feed. The decomposition proceeds enzymatic or with the participation of anaerobic bacteria [1, 3, 4]. Gases removed by ventilation contain also dimethylamine, carbon monoxide and dioxide, aldehydes, ketones, organic acids and many other organic compounds belonging to odours [3–7].

High concentration of ammonia increases birds susceptibility to diseases, causes inflammation of eyes mucous membrane, problems with respiration and decreases a body mass increment [5, 6]. The main sources of ammonia are as follows:

- direct emission from poultry houses,
- places where litter and droppings are stored,
- cultivated field during poultry manure distribution [8–12].

The most important aim in the limitation of ammonia emission is maintenance of hygiene at the high level in the poultry house as well as equipment of efficient ventilation system. Well designed ventilation system prevents concentration of gases in the building and keeps temperature and humidity at the level which guarantees good mood and health of birds [1, 4].

Stock-farming is accompanied also by emission of different gases which causes air pollution and noxiousness of odours. The sources of gaseous pollutants are animals, their droppings, feeds and technological systems. Animals emit first of all carbon dioxide, and methane and odours gases (sulphur organic compounds, aromatic hydrocarbons, organic acids, aldehydes, etc.) in lower amounts. Animal droppings are the source of ammonia which is the most noxious gas in this farming [1, 4, 9–20].

Experimental

Polluted air in a big farm of poultry keeping (~18 thousands of chickens) in Łodz province was sampled. The aim of the investigation was to determine odour pollutants, especially ammonia, in air and check the possibility of a catalytic method application in their removal [2–4]. Gases sampling was carried out in the central part of the building (Fig. 1) and near outlets of ventilators at the height of 0.5 m [17–21], in the period of poultry fattening – 5th and 6th week of the keeping, at various day-times and seasons.

Fig. 1. Poultry house inside

Gases containing odours from milker cows farming were sampled in one farm building with two series of places for animals, taken up by 30 milker cows and in the septic tank collecting outflows from this building. The cowhouse length, width and average height was 25, 12.5 and 2.6 m inside, respectively. Cubic capacity of this building was 840 m^3. The building was equipped with roof and side natural ventilation and fulfilled domestic and EU requirements. The septic tank was located behind the cowhouse and its dimensions were as follows: length – 11 m, width – 4 m, height – 2 m. This tank was filled up to one third of its volume during sampling.

Gas samples were analyzed on the spot of sampling with an application of gases analyser Madur GA-20, as well as in a laboratory with an application of spectrophotometric methods and gas chromatography (GC-MS). Colorimetric or spectrophotometric analyses included the determination of ammonia [22–24], hydrogen sulphide [25] and formaldehyde [26]. The intensity of odours was estimated using five-stage scale applied by local authorities in Japan for odorous protection of air quality. Table 2 presents concentration values of 4 among 8 obligatory air pollutants (ammonia, methanethiol, hydrogen sulphide, dimethyl disulfide, trimethylamine, acetaldehyde and styrene), which determine potential harmfulness on five-stage scale applied by local authorities in Japan for determination of the highest allowable concentrations of odours in the environment [3]. The intensity of odour in air in work-places, as well as in air outside production buildings should not be higher than 3.5 stage (for ammonia 3.55 mg/m^3) which is the upper level (clear) of this stage.

Table 2

A dependence of odour intensity on concentration of selected odours applied by local authorities in Japan during determination of the highest allowable concentrations [3]

Odour intensity		Odour concentration				
		[ppm]				[mg/m^3]
		Methanethiol CH_3SH	Acetaldehyde CH_3CHO	Styrene $C_6H_5CHCH_2$	Ammonia NH_3	Ammonia NH_3
1	Detection threshold	0.0001	0.002	0.03	0.1	0.07
2	Recognition threshold	0.0007	0.01	0.2	0.5	0.36
2.5	Clear	0.002	0.05	0.4	1	0.71
3.0		0.004	0.1	0.8	2	1.42
3.5		0.01	0.5	2	5	3.55
4	Strong	0.03	1	4	10	7.10
5	Extreme strong	0.2	10	20	40	28.4

Results and discussion

Selected results of the pollutants determination in air from the poultry keeping farm (poultry house) and cowhouse with milker cattle are presented in Tables 3–5 and Tables 6–7, respectively.

The presence of ammonia was found inside the poultry house at varying concentrations in the range from 0.82 to 2.65 mg/m^3 (Tables 3–5). Results of the analyses show that the ammonia concentration inside the building was a little bit higher at noon and in the evening. The ammonia concentration was only 0.26 mg/m^3 (Table 5) in the air removed from the poultry house by the outlet of the side ventilator. Chromatographic analyses in the GC-MS system did not show ammonia content higher than 0.1 % or organic compounds concentrations higher than 1 mg/m^3 possible for the detection in this system. Carbon monoxide, sulphur dioxide, hydrogen sulphide (> 2.0 mg/m^3) and formaldehyde (> 0.25 mg/m^3) was not detected. Traces of dust (not detected) arising from the building and covering ventilators casing or plants below their outlets, were observed.

Significant concentrations of ammonia (3.2–5.6 mg/m^3) were determined in the cowhouse also in the height of 0.5 m above the sewer with temporary stored manure (Table 6). An increase in this odour concentration to 15.5 mg/m^3 (Table 6) occurred during mechanical removal of manure (twice a day). The ammonia content in air was the highest inside the septic tank and totalled 18.8 mg/m^3 (Table 7).

Table 3

Analysis results of air sampled in a large building of the poultry keeping farm [16]

Analysed component	Measurements – 24.09.2009 (midday). Air temperature inside the building 24 °C and outside the building 19 °C		Measurements – 01.10.2010 (evening). Air temperature inside the building 22 °C and outside the building 9 °C	
	Air in the central part of the building at the height of 0.5 m	Air at the outle of a ventilator	Air in the central part of the building at the height of 0.5 m	Air at the outlet of a ventilator
O_2 [%]	20.5	20.9	20.9	20.9
CO_2 [%]	0.3	0	0	0
CO [ppm]	0	0	0	0
NH_3, mg/m^3	1.45–2.59	N.d.*	0.82–1.37	N.d.
Formaldehyde [mg/m^3]	< 0.25	< 0.25	< 0.25	< 0.25
Odour intensity: stage; description	3.0; clear	3.5; clear	2.5; clear	3.0; clear

* N.d. – not determined.

Table 4

Analysis results of air sampled inside the poultry house on November 30, 2009 (midday). Air temperature in the poultry house 22 °C and outside 6 °C

Analysed component	Analysis of gases supplied to a laboratory	Analysis of sorptive solutions collected in gas washers [16]	Air at the outlet of a ventilator [16]	Air in a distance of 10 m from the outlet of a ventilator [16]
O_2 [%]	20.5	—	20.5	20.9
CO_2 [%]	0.3	—	0.3	0
CO [ppm]	0	—	0	0
SO_2 [ppm]	0	—	0	0
TOC in a solution in a gas washer [mgC/dm^3]	—	2.493	—	—
NH_3 [mg/m^3]	1.29–2.39	1.97–2.65	N.d.	N.d.
Formaldehyde [mg/m^3]	< 0.25	N.d.	< 0.25	N.d.
Hydrogen sulphide [mg/m^3]	< 2.0	N.d.	< 2.0	N.d.
Odour intensity: stage; description	< 3.0; clear	—	3.5; clear	2.0–2.5; recognition threshold – clear

Air sampled in the poultry house, cowhouse and septic tank contained carbon dioxide in the concentration range 0–0.3 % and oxygen in the concentration range 20.5–20.9 %, determined using automatic gas analyser Madur GA-20. Carbon monoxide and sulphur dioxide were not detected. These pollutants are often present in gases emitted from municipal wastes dumps and fermented wastewater sludge, in which microbiological processes occurs under anaerobic conditions or under oxygen deficiency.

Table 5

Analysis results of air from the poultry keeping farm on May 25, 2010 (morning). Air temperature inside the building 22 °C and outside 20 °C [16]

Analysed component	Air sampled inside the poultry house at the height of 0.5 m from the ground	Air removed from the inside of the poultry house and sampled at the side ventilator outlet
O_2 [%]	20.9	20.9
CO_2 [%]	0	0
CO [ppm]	0	0
SO_2 [ppm]	0	0
CH_4 [ppm]	1.0	0
NH_3 [mg/m^3]	0.84–1.19	0.26
Formaldehyde, mg/m^3	< 0.25	< 0.25
Hydrogen sulphide [mg/m^3]	< 2.0	< 2.0
Odour intensity: degree; description	3.0–3.5; clear	2.5–3.0; clear

Table 6

Analysis results of air sampled inside the cowhouse before and during removal of manure from the storing sewer in March 17, 2010. Air temperature inside the cowhouse was 18 °C

Analysed component	Air inside the cowhouse sampled at the height of 0.5 m, before manure removal	Air inside the cowhouse sampled at the height of 0.5 m, during manure removal
O_2 [%]	20.9	20.9
CO_2 [%]	0	0
CO [ppm]	0	0
SO_2 [ppm]	0	0
NH_3 [mg/m^3]	3.2–5,6	15.5
TOC of a solution in a scrubber [mgC/dm^3]	5.961	6.342
Formaldehyde [mg/m^3]	< 0.25	< 0.25
Hydrogen sulphide [mg/m^3]	< 2.0	< 2.0
Odour intensity: stage; description	3.0–3.5; clear	3.5–4.0; clear – strong

Odour intensity was estimated using five-stage scale developed in Japan with the third stage splitted for three levels labelled as: 2.5, 3.0 and 3.5 (clear). The measurements proved that odour intensity in the air inside the poultry house and removed by the ventilators was the highest in the third stage, *ie*, clear, and reached the value of 3.5. The odour intensity decreased quickly with an increase in the distance from the ventilator in spite of air flow in the same direction (2–3 m/s), because in the

Table 7

Analysis results of air sampled inside the septic tank in March 17, 2010.
Air temperature outside and inside the septic tank was 4 and 8 °C, respectively

Analysed component	Air sampled inside the septic tank
O_2 [%]	20.9
CO_2 [%]	0
CO [ppm]	0
SO_2 [ppm]	0
NH_3, mg/m^3	18.8
TOC of a solution in a scrubber [mgC/dm^3]	5.362
Formaldehyde [mg/m^3]	< 0.25
Hydrogen sulphide [mg/m^3]	< 2.0
Odour intensity: stage; description	4.0; strong

distance of about 10 m, this intensity was only at the level of the stage limit – recognition threshold and clear, *ie*, 2.0–2.5. Odour intensity in the cowhouse was at the level of 3.0–3.5 (clear) but it increased to the level of 4 (strong) during removal of manure.

Summary

Within sampling period, poultry keeping in the farm was the source of variable in time ammonia emission ranging from 0.82 to 2.65 mg/m^3. Higher concentrations of ammonia (3.2–5.6 mg/m^3) were determined in air sampled in the cowhouse. Temporary increase in ammonia concentration to 15.5 mg/m^3 occurred during removal of manure. However, the highest concentration (18.8 mg/m^3) was determined in the underground septic tank. Air inside in farm contained carbon dioxide (0–0.3 %) and oxygen (20.5–20.9 %). Concentrations of ammonia determined in the poultry house in the evening were lower than in the morning and at noon.

Carbon monoxide, sulphur dioxide, hydrogen sulphide (> 2.0 mg/m^3) and formaldehyde (> 0.25 mg/m^3) was not detected. The highest odour intensity inside the building of chicken keeping and at outlets of ventilators was at the third stage in odour scale applied in Japan (3.5), *ie*, clearly perceptible. However, it decreased significantly with the increase in a distance from the building. Odour intensity in the cowhouse was at the level of 3.0–3.5 (clear) and increased to the level of 4 (strong) during removal of manure.

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OZNACZANIE AMONIAKU I INNYCH ZANIECZYSZCZEŃ W POWIETRZU NA TERENIE FERM HODOWLI DROBIU I KRÓW MLECZNYCH

Instytut Chemii Ogólnej i Ekologicznej
Politechnika Łódzka

Abstrakt: Wykonano pobory próbek zanieczyszczonego powietrza z dużej fermy drobiu rzeźnego (~18 tys. kurcząt) oraz budynku hodowli bydła mlecznego (30 zwierząt) w województwie łódzkim. Celem badań było wykonanie analiz powietrza na zawartość zanieczyszczeń odorowych, zwłaszcza amoniaku, a w perspektywie zbadanie możliwości zastosowania metody katalitycznego utleniania do ich usuwania. Próbki gazów były analizowane na miejscu pobierania za pomocą automatycznego analizatora gazów Madur GA-20, a także w laboratorium metodami instrumentalnymi i spektrofotometrycznymi. Do oceny intensywności zapachu zastosowano pięciostopniową skalę wykorzystywaną przez władze lokalne w Japonii do ochrony zapachowej jakości powietrza. Hodowla drobiu w badanej fermie była w okresie pobierania źródłem zmiennej w czasie emisji amoniaku w granicach 0,82–2,65 mg/m^3. W powietrzu obiektu stwierdzono 0–0,3 % ditlenku węgla i 20,5–20,9 % tlenu, natomiast nie wykryto tlenku węgla, ditlenku siarki, siarkowodoru (> 2,0 mg/m^3) ani formaldehydu (> 0,25 mg/m^3). Największa intensywność zapachu wewnątrz budynku hodowli kurcząt, a także na wylotach wentylatorów była w trzecim stopniu skali zapachu stosowanej w Japonii (3,5), tj. wyraźna, jednak znacznie obniżała się wraz z oddalaniem się od obiektu. Znaczniejsze były stężenia amoniaku w powietrzu budynku hodowli bydła mlecznego, które mieściły się w zakresie 3,2–5,6 mg/m^3. Wyższe było stężenie chwilowe amoniaku podczas usuwania obornika 15,5 mg/m^3, a najwyższe w gazach nad gnojowicą w zbiorniku szamba 18,8 mg/m^3.

Słowa kluczowe: fermy drobiu, oznaczanie amoniaku, obora bydła mlecznego, odory w produkcji rolnej

Renata GNATOWSKA[1]

NUMERICAL MODELING OF POLLUTION DISPERSION AROUND THE OBJECTS IN TANDEM ARRANGEMENT

NUMERYCZNE MODELOWANIE ROZPRZESTRZENIANIA SIĘ ZANIECZYSZCZEŃ GAZOWYCH WOKÓŁ OBIEKTÓW W KONFIGURACJI TANDEM

Abstract: The dispersion of pollutants in space around wind engineering structures governed by convection and diffusion mechanism and depends strongly on the velocity field. To understand the phenomena related to the forming of concentration fields it is necessary to recognize the local features of the flow around the objects with the special emphasize for the mean velocity direction, random and periodical fluctuations accompanying the vortex generation in bodies neighbourhood. The specific flow conditions generated around bluff bodies arrangement make it possible to study the gas pollutant dispersion for the case of very complex velocity field typical for built environment.

This paper evaluates the performance of computational modelling approach (RANS k-ε) for two test cases with wind tunnel experiments for validation. The paper presents the results of the complex research program aimed at understanding a character of the flow field in neighborhood of bluff-bodies immersed in a boundary layer and characteristics of pollutants dispersion in that area. The analysis has been performed for the 3D case of two surface-mounted bluff bodies arranged in tandem. The local characteristics of flow and concentration profiles of tracer gas (CO_2) for various inter obstacle gaps were obtained by the use of commercial CFD code (FLUENT). Characteristic feature of flow field around groups of buildings in urban areas is high level the unsteady phenomena resulting from itself character of the wind or from the interference of the wake flow connected with a process of vortex shedding. This is the factor affecting process of the dispersion of pollutants in the built-up area acting more complex the mechanism of propagate of small parts explained on the basis of processes of advection and turbulent diffusion.

Keywords: numerical modeling of pollution dispersion, buildings arrays

The pollutant dispersion in urban areas can have negative consequences on health and comfort of their inhabitants, and on the built environment.. Understanding the transfer and deposition of pollutants in the urban environment is therefore essential in the design process of a building or a ventilation system. Ensuring adequate air quality requires proper aeration of these areas. Its efficiency depends mainly on arrangements of the buildings, the wind direction and locations of emissions sources. The process of

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[1] Institute of Thermal Machinery, Technical University of Czestochowa, al. Armii Krajowej 21, 42–201 Częstochowa, Poland, phone: +48 34 325 05 34, email: gnatowska@imc.pcz.czest.pl

pollution dispersion is mainly influenced by mechanisms of mass diffusion, caused by concentration gradients and advection which transfers pollutants in flow direction through mean air movement. Another important factor affecting the entrainment of pollutants into and out of the wake region is the unsteadiness of the wake caused by the shedding of corner vortices. Important role is also played by turbulent transport processes [1, 2]. Improvement in air quality on a local scale and limitation of effect of pollution on human health requires consideration of all the listed factors.

Amongst the methods commonly used to establish better understanding of the wind flow and dispersion processes in the atmospheric boundary layer, *computational fluid dynamics* (CFD) is increasingly explored. Due to the turbulent nature of the wind flow around buildings, the accuracy of the CFD approach applied to urban dispersion problems is to a large extent determined by the performance of the turbulence approach and turbulence model used.

This paper presents the numerical tests of the qualification of the relation between a structure of the flow field in complex urban terrain and characteristics of pollutants dispersion. The *Reynolds Averaged Navier-Stokes* (RANS) turbulence modeling approaches have been used with the k-ε model in RNG version. This choice is made following the work of Baik et al [3] who studied the dispersion of reactive pollutants in an urban street canyon with use the RNG k-ε turbulence model and shows good agreement between the numerical simulation and wind tunnel experiment. The numerical results are compared with experimental data presented in previous article [4]. The aim of the study was to determine the impact of objects configuration, their degree of "immersion" in the boundary layer for the spread of the tracer gas emitted in the vicinity of two cubes in tandem arrangement.

Methods of analysis

Description of the case study

The geometries of the analyzed cases of two obstacles and location of the source in relation to the investigated arrangement of the objects as well as the assumed coordinate system are presented in the Fig. 1. All the measurements were carried out for the

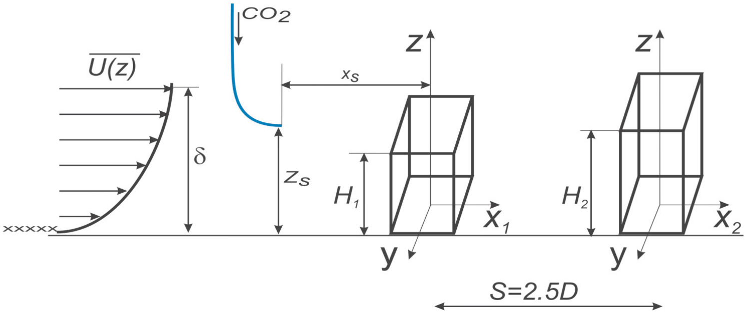

Fig. 1. Schematic diagram of objects in tandem arrangement used in the numerical simulations and nomenclature

Reynolds number $Re_D = 3.4 \cdot 10^4$ based on the free stream velocity $U_\infty = 13$ m/s. The source of emission of carbon dioxide used as a gas marker during the investigations was a pipe located on the symmetry line of the objects at the distance of $x_s = -2.5$ D and at the height $z_s = H_1$ before the windward one. The CO_2 emission rate was assumed $Q = 5$ dm^3/min.

The results of study presented in this work relate to a fixed ratio of object height $H_1/H_2 = 0.6$ and different "immersion" in boundary layer $H_2/\delta = 0.6$, $H_2/\delta = 1.0$.

RANS with the RNG k-ε model

The program of this work consists of comparison of pollutant concentration profiles (obtained as a result of numerical simulation) with aerodynamic characteristics for building-downwash effect. Three-dimensional RANS simulations have been carried out using a commercial CFD code, FLUENT v.6.3, with the RNG version of a k-ε turbulence. According to the literature [4, 5] this model is widely used for flows in a build environment. For the considered configuration the experimental verification of numerical data has been performed in wind tunnel, which details and results were presented in previous article [4]. When using this model in the present study, the momentum, k and ε transport equations are discretized using a second order upwind scheme. Pressure interpolation is performed with a second order scheme. The SIMPLE algorithm is used for pressure-velocity coupling.

In the CFD simulations presented in this paper, the profiles of longitudinal velocity, k and ε are prescribed at the inlet of the domain (Fig. 2). The oncoming flow profiles have been approximated using the power distribution $U(z) = U_\delta\ (z/\delta)^\alpha$ where α characterizes the terrain type. In addition to the inlet velocity profile, the k-ε RNG

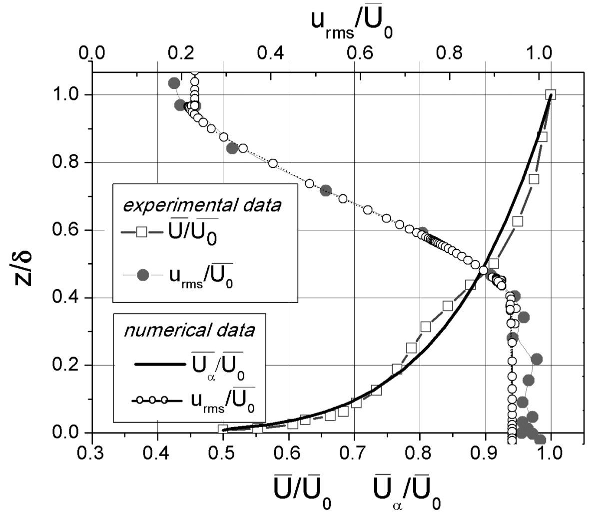

Fig. 2. Distribution of mean velocity U and velocity fluctuations u_{rms} measured in the wind tunnel and implemented as inflow conditions in numerical simulations

turbulence model requires an appropriate distribution of the turbulent kinetic energy k and the dissipation rate ε which together define the velocity and length scale of the turbulent motion. Different definitions of inlet boundary conditions have been analyzed and compared with experimental data [6]. The profiles of U, k and ε that are prescribed at the inlet of the domain are based on the wind tunnel measurements. One of the best methods to describe the inlet boundary conditions is the method proposed by Richards and Hoxey [7]. This, method has been accepted for the calculations described in this paper.

At the outlet, condition "pressure outlet" – provides a uniform distribution of static pressure is prescribed. At the top and lateral boundaries, a symmetry boundary condition is imposed. The domain dimensions have been determined following the COST 732 guidelines (Franke et al, 2007 [8]): 30D (length) · 10D (width) · 10D (height). In the streamwise direction, an empty distance of 6.5D and 20D is allocated upstream and downstream the buildings, respectively. The three-dimensional CFD domain consisted of two objects with a square base (0.04 × 0.04 m) and different heights. The grid independent solution has been obtained for by systematically refining the entire mesh in each direction, increasing the number of nodes by about 50 %. The resolution for tandem arrangement objects has been 298 × 130 × 70. Figure 3 shows the mesh used in the present simulations for a dual objects configuration.

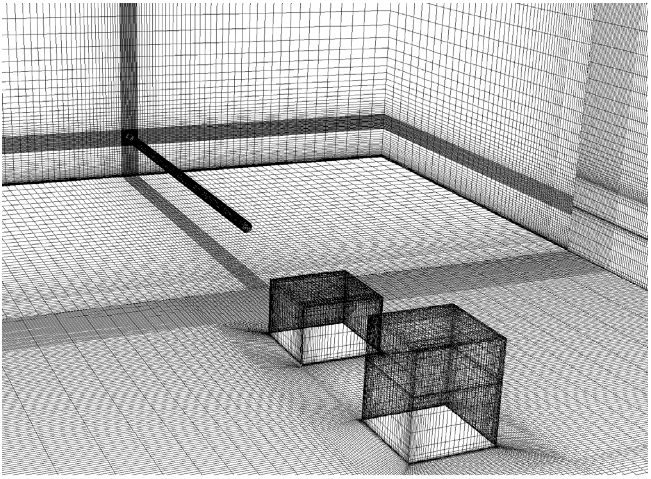

Fig. 3. The computational mesh for objects in tandem arrangement with parameters $H_1/H_2 = 0.6$, $H_2/\delta = 0.6$, $z_S = H_1$

Discussion of the results

The analysis of gas pollution dispersion process requires in-depth identification of the structure of flow around the buildings. The flow structure around three-dimensional bluff-body located on the surface with formed boundary layer is characterized by a high level of complexity.

The case under consideration in this work concerns tandem arrangement which is characterized by H_1/H_2 parameter, which is conducive to occurrence of so-called "downwash" effect $H_1/H_2 = 0.6$. This effect consists in washing of front side of the leeward object with large air masses, which results in strong air circulation in the area between objects, which determines flow structure between them. The zone typical of flow between cuboids are clearly visible in the Fig. 4. The level of modification of flow around the objects of tandem arrangement depends on many factors (distance between elements, change in height of the objects, immersion parameter in boundary layer). In the case of the tandem arrangement, being considered here, in addition with "downwash" effect the arrangement low-height elements can contribute to the intensification of mixing processes and consequently lead to improved air quality at the zone between objects as it was pointed out by Vanweert and van Rooij [9]. Appropriate design of the wind environment with the presence of emission sources is very important especially taking into account human health and life comfort.

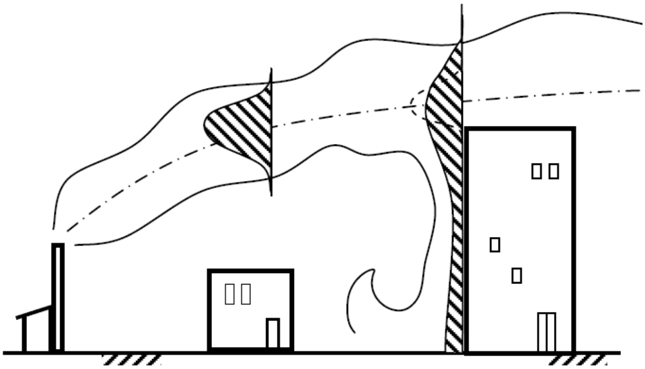

Fig. 4. Scheme of the flow pattern obtained on the base the smoke visualization

The observed modifying impact of interaction between the objects in tandem arrangement is reflected in the results of concentration of the tracer gas emitted in their environment. The Fig. 5 presents the longitudinal component of mean velocity contours distribution in the plane y/D = 0. In order to ensure proper comparison of the results, one should reduce the analysed values with the values measured in the place of build-up of the objects. A reference value is the value of velocity registered at the height H_1 in undisturbed flow in the place of object build-up U_{H_1}. Flow around objects with varied height and flow of air from the side of lower element $H_1/H_2 = 0.6$ is conducive to occurrence of downwash effect. This effect is characterized by strong air circulation in the zone between objects, totally determining the structure of flow between each other. Strong air circulation between objects determines rise in velocity of the factor with the direction opposite to the direction of flow of main wind directly adjacent to the ground. No considerable difference in the structure of flow behind the system was observed in the analysed cases. In all the analysed configurations, the air detached on windward wall in first element is detached again in the second object. Renewed detachment of

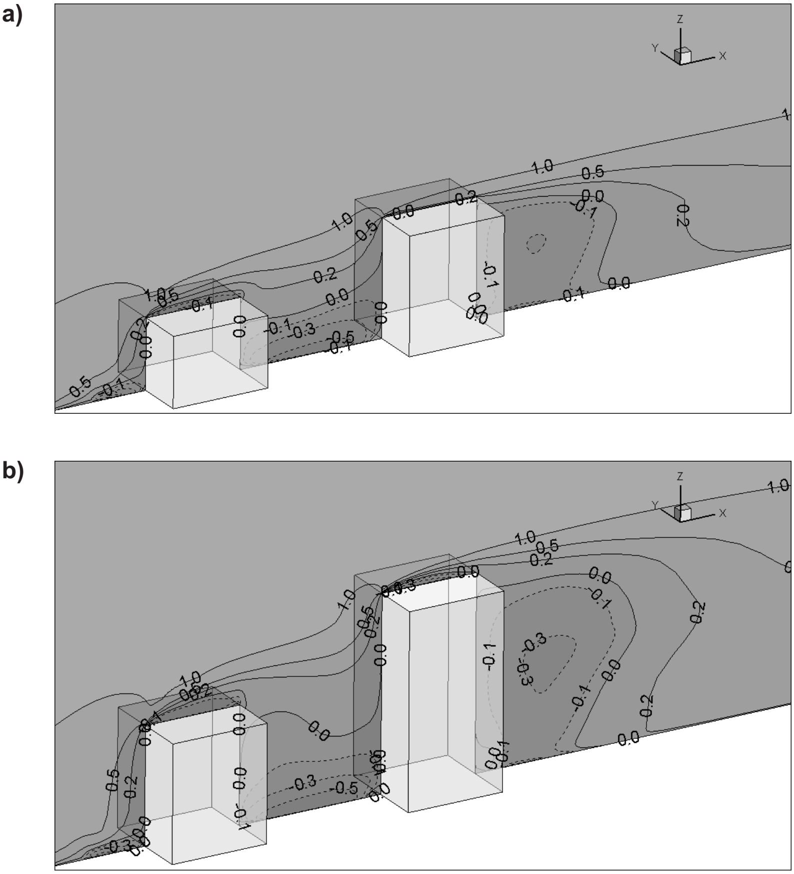

Fig. 5. The contour of longitudinal component of mean velocity U/U_{H_1} in the symmetry plane: a) $H_2/\delta = 0.6$; b) $H_2/\delta = 1.0$

flow from upper surface of the leeward element causes that the length of recirculation zone behind the system remains actually unchanged.

Disturbing impact of the second object on the CO_2 distribution around the analysed arrangement of cubes is illustrated in next figures which shows the distribution of CO_2 concentration in and behind the objects gap for the considered configurations. The general behavior of the concentration fields in numerical and experimental measurements are similar. Fig. 6 and 7 presents cross-sectional distribution of concentration in the gap between objects for both considered configurations: as experimental and numerical results, respectively. The numerical simulations are verified by the experiments performed by Gnatowska and Moryn [4].

It can be seen the high value of the gas marker concentration, emitted at the height of the windward object, at a certain distance from the source and a decrease along the flow direction. The gas marker is moved mainly through upper flow. When the CO_2 plume arrives to front side of the leeward object, which results the strong value of

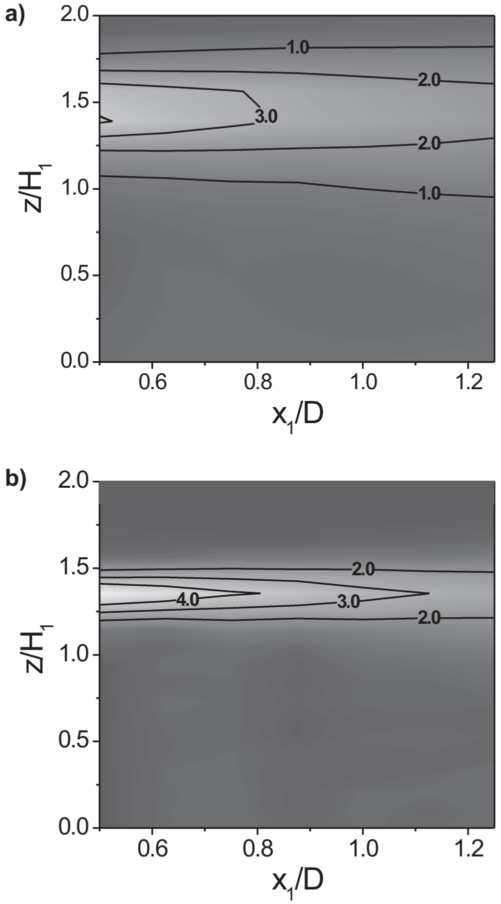

Fig. 6. Experimental measurement – Distribution of mean concentration CO_2 ($z_S = H_1$; $y/D = 0$) in the inter-obstacle gap for different the immersion parameter: a) $H_2/\delta = 0.6$; b) $H_2/\delta = 1$

concentration in that area. The images that we can observed between objects are the result of the flow structure between them. This situation is confirmed in figures, which shows the lower values of pollutant concentration behind the array of two cuboids. It is caused by the recirculation bubble in the gap region between objects in tandem.

Change in height of the elements of the arrangement impacts on changes in the immersion parameter in boundary layer. As results, the biggest changes in flow field are observed in the area between objects. Rise in object height in relation to layer thickness causes rise in impact of windward object and increase in width and length of recirculation zone and extension of the area taken by vortices.

General the numerical results are agreed well with experimental data, but the main observation from all two cases is that the numerical simulations little overestimate the cross-wind (lateral) dispersion of the pollutants. The differences appear practically for each location of the measuring traverse. Further investigation should be directed

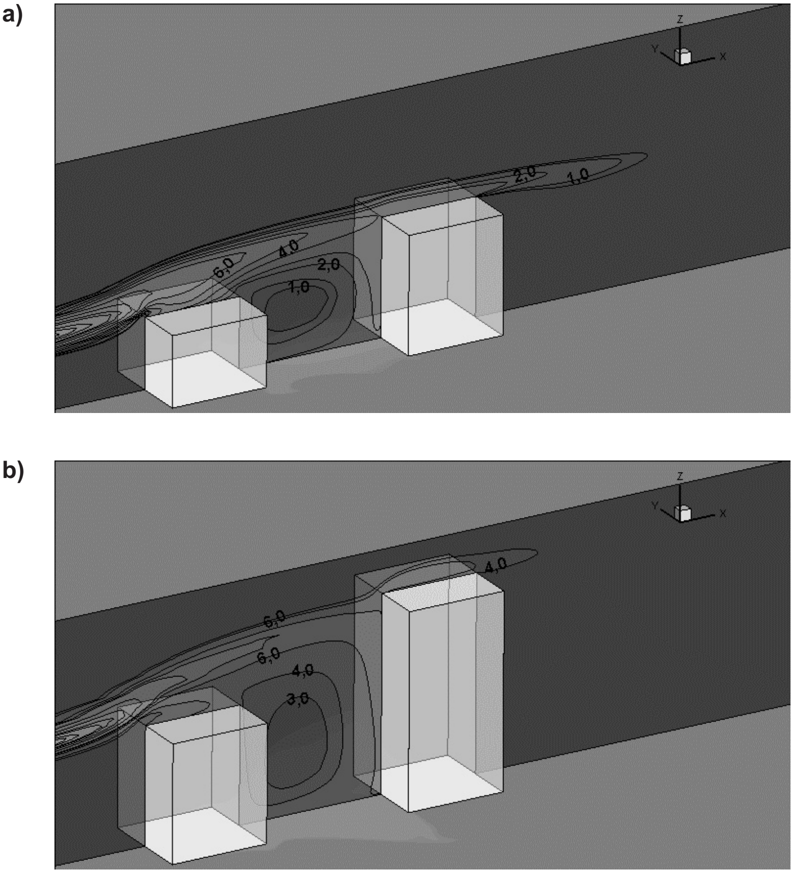

Fig. 7. Numerical simulation – Distribution of CO_2 Mass Fraction [%] ($z_S = H_1$; $y/D = 0$) in the inter-obstacle gap for different the immersion parameter: a) $H_2/\delta = 0.6$; b) $H_2/\delta = 1$

towards identifying the main reasons for numerical modelling discrepancies based on idealized case studies, to support future more complex case studies.

Conclusions

The performed numerical research was aimed primarily at the development of the existing knowledge of the interaction between objects located on the ground and its influence on the pollutant dispersion.

In present experimental study of CO_2 concentration fields around bluff-bodies in tandem arrangement have been observed for case so-called “downwash” effect $H_1/H_2 = 0.6$. The results of the present work showed good agreement between the results of numerical simulation and the wind tunnel experiments for both wind flow and concentration field. Velocity field obtained from the RNG k-ε turbulence model shows the reverse flow in the gap between objects and in the near wake region.

In upper part of first building and between them occurs high level of pollution dispersion, which slowly reduces as the plume moves up the behind objects agreement. The diffusion concentration was very high near the source location. The concentration results with the RNG k-ε model were observed in agreement with the wind tunnel results. The area of maximum concentration is wide, occupying the width of the building.

The numerical simulation results indicate that differences in flow and pollutant dispersion strongly depend on building configuration. A further systematic investigations for various building arrays are needed. Also, a study is required to explain reasons for the variations in flow and pollutant dispersion.

Acknowledgements

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NUMERYCZNE MODELOWANIE ROZPRZESTRZENIANIA SIĘ ZANIECZYSZCZEŃ GAZOWYCH WOKÓŁ OBIEKTÓW W KONFIGURACJI TANDEM

Instytut Maszyn Cieplnych
Politechnika Częstochowska

Abstrakt: Rozprzestrzenianie się zanieczyszczeń w przyziemnej warstwie atmosferycznej regulowane jest przez mechanizm dyfuzji i konwekcji oraz silnie zależy od pola prędkości. W celu zrozumienia zjawisk związanych z kształtowaniem się pól koncentracji istotne jest rozpoznanie struktury przepływu wokół obiektów ze szczególnym uwzględnieniem prędkości średniej oraz jej losowej i okresowej składowej towarzyszącym generacji wirów w otoczeniu obiektów naziemnych w obszarach zabudowanych.

W pracy przedstawiono wyniki numerycznego modelowania procesu dyspersji zanieczyszczeń gazowych w strefie zabudowanej. Ich celem było określenie wpływu konfiguracji obiektów, stopnia ich „zagłębienia" w warstwie przyziemnej, a także położenia źródła emisji na rozprzestrzenianie się zanieczyszczeń (znacznik gazowy – CO_2). Badany układ stanowiły dwa trójwymiarowe modele budynków o różnych wysokościach ustawione w tandemie. Charakterystyki aerodynamiczne przepływu oraz profile koncentracji gazu znacznikowego (CO_2) dla różnych konfiguracji obiektów uzyskano z wykorzystaniem komercyjnego oprogramowania FLUENT. Cechą szczególną pól prędkości w otoczeniu grupy opływanych budynków jest wysoki poziom niestacjonarności wynikający zarówno z samego charakteru wiatru, jak i z faktu generowania przez obiekty zjawisk periodycznych związanych z procesem schodzenia wirów. Jest to czynnik, który oddziałuje na proces dyspersji zanieczyszczeń w obszarze zabudowanym, czyniąc jeszcze bardziej złożonym mechanizm rozprzestrzeniania się cząstek tłumaczony na bazie procesów adwekcji i turbulentnej dyfuzji.

Słowa kluczowe: numeryczne modelowanie dyspersji zanieczyszczeń, układy budynków

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Aleksandra PŁATKOWSKA-SIWIEC[1*] and Michał BODZEK[1]

INFLUENCE OF WATER PROPERTIES ON FOULING INTENSITY AND FOULING MECHANISM DURING ULTRAFILTRATION

BADANIE WPŁYWU WŁAŚCIWOŚCI WODY NA INTENSYWNOŚĆ I MECHANIZM ZJAWISKA FOULINGU W PROCESIE ULTRAFILTRACJI

Abstract: Membrane techniques are an alternative water treatment method for classical processes. However, mostly their capacity and membrane lifetime are limited by the phenomenon called fouling, *ie* the accumulation of organic and/or inorganic substances on the surface and into the pores of the membrane. The results of the study presenting the dependence of water properties such as pH, kind of organic matters and ionic strength on membrane fouling are discussed in this article. *Unified Modified Fouling Index* (UMFI) was used to describe intensity of fouling. Also the influence of water properties on fouling mechanism are shown.

Keywords: ultrafiltration, NOM, fouling, pH, ionic strength

Both, inorganic and organic substances are present in surface waters. The Regulation of Minister of Environment in Poland on quality of surface waters used as drinking water supply [1] defines permissible pH, water hardness, concentrations of chlorides, sulphates and total organic carbon content. The classical water treatment methods *ie* coagulation, bed filtration, oxidation can be replaced by membrane processes. The main exploitation problem connected with low-pressure membrane techniques is the decrease of membranes capacity caused by fouling phenomenon. Different mechanisms of fouling can appear during the process. According to Hermia's model, the constant pressure filtration law can be described as:

$$\frac{d^2t}{dV^2} = k\left(\frac{dt}{dV}\right)^n \tag{1}$$

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[1] Division of Sanitary Chemistry and Membrane Processes, Institute of Water and Wastewater Treatment, Faculty of Energy and Environmental Engineering, Silesian University of Technology, ul. S. Konarskiego 18, 44–100 Gliwice, Poland, phone: +48 32 237 29 81, email: aleksandra.platkowska@polsl.pl

where: V – permeate volume;
t – filtration time;
n, k – constants typical for different fouling mechanisms.

Constant flux membrane processes are most often apply in the industry. Analogically to the Hermia's model, such processes can be described as follows:

$$\frac{dP'}{dV_s} = k_v P' n \tag{2}$$

where: P' – the ratio of the transmembrane pressure to the normal pressure [-];
V_s – cumulated permeate volume per unit membrane area [$\mathrm{m^3/m^2}$];
k_v, n – constants typical for different fouling mechanisms.

Huang et al [2] derived the formula, which can be applied for both, constant pressure and constant flux filtrations:

$$-\frac{dJ'_s}{dV_s} = k_v {J'_s}^{2-n} \tag{3}$$

where: J_s' – specified normalized permeate flux [-],
k_v (UMFI) – fouling parameter [$\mathrm{m^2/m^3}$].

General solutions of differential equation (3) depending on the fouling mechanism are shown in Table 1, where C – the integration constant. The slope of the straight line to the x axis determine the intensity of fouling and is called *Unified Modified Fouling Index* (UMFI). The introduction of normalized flux to the equation 3 allows to compare membranes with different separation properties (stream, porosity), while the introduction of V_s allows to compare the laboratory scale results with the industrial scale studies.

Table 1

Filtration laws – general solutions of differential equation

Mechanism	Solution equation
Standard bloking	$2\sqrt{J_s} = C - \mathrm{UMFI} \cdot V_s$
Complete bloking	$J_s' = C - \mathrm{UMFI} \cdot V_s$
Intermediate bloking	$\ln J_s' = C - \mathrm{UMFI} \cdot V_s$
Cake formation	$\frac{1}{J_s'} = C + \mathrm{UMFI} \cdot V_s$

According to Hermia's model following fouling mechanisms can be distinguished:

– standard blocking – the contraction of membrane pores caused by the adsorption which occur during the filtration; particles can block inside of pores depending on differences between pores shape and adsorbate particles shape;

– complete blocking – the blocking of pores on the membrane surface, however particles do not overlay on each other;

– intermediate blocking – the blocking of pores on the membrane surface, however particles cumulate one on another;

– cake or gel formation – the accumulation of substances on the membrane surface (particles do not penetrate the membrane interior), particles form precipitate or gel of different density degrees [3–6].

The fouling intensity depends on both, membrane and feed water properties. The ionic strength and pH influence on the solubility of organic substances present in water, and additionally, they can change interactions between particles and membrane surface. Properties of organic substances are also important. Chemical character and structure of organic particles are quite significant when transport through the membrane is considered. Linear particles of aliphatic structure are easier transported through the membrane pores than the cyclic ones. On the other hand, aliphatic particles are much easier adsorbed in pores what leads to the irreversible fouling, while cyclic compound can precipitate on the membrane surface and cause the reversible fouling appearance [7].

The aim of the study was to determine the influence of pH, ionic strength and type of chemical substances on UMFI value for different fouling mechanisms as well as on the degree of removal of organic substances.

Material and methods

The study were carried out in Ultrafiltration Cell Millipore CDS10 System. CDS10 device cooperated with flat sheet membranes and the dead-end mode filtration was performed. The feed was introduced perpendicularly to the membrane surface. The applied pressure was kept constant and equal to 0.1 MPa. The scheme of the ultrafiltration system was presented in [8]. The new membrane was used in every experiment. The characteristic of applied membranes is presented in Table 2. The molecular weight cut off was defined by the membrane producer.

Fluxes of deionized water and contact angles were determined for all new membranes. Measurements of the contact angle were done using the goniometer and the sessile drop method was applied. The angle between drop of water, membrane surface and air was measured.

Table 2

The characteristics of membranes (J_m – water flux)

Producer	KOCH Membrane Systems
Membrane material	Poly(vinylidene fluoride) (PVDF)
MWCO [kDa]	30
Contact angle [^{o}]	57.5 ± 5.2
J_m [dm^3/hm^2] (t = 20 ^{o}C)	94

The absolute value of UMFI was applied to describe the intensity of fouling during ultrafiltration. Simulated waters containing humic substances (2–500) kDa and dextranes (3–110) kDa were used in the study. The intensity of fouling and the ultrafiltration effectiveness were determined for waters:

– of constant humic substances and dextranes mass ratio ($x_{H/D} = 0.5$) and with low ionic strength and various pH (5–9),

– of constant humic substances and dextranes mass ratio ($x_{H/D} = 0.5$) under constant pH equal to 7 and various calcium ions concentrations (0–200) mg/dm^3,

– of constant pH equal 7, low ionic strength and different composition of organic substances (different mass ratios of humic substances and dextranes, SUVA = (0.66–7.05) m^2/g C.

In order to determine the reversibility of fouling phenomenon the backflushing of membrane was performed and the percentage recovery of initial deionized water flux was defined.

Results and discussion

The fouling intensity was characterized by means of the modulus of Unified Modified Fouling Index. Least Squares Estimation was used to determine UMFI. Table 3 presents correlation coefficients (R) obtained for particular filtrations together with UMFI absolute values and uncertainty of measurements of UMFI.

Table 3

The statement of UMFI obtained during particular filtrations

pH [-]	Ca [mg/dm^3]	x_H [-]	Cake formation		Complete blocking		Interdirect blocking		Standard blocking	
			UMFI × 10^3 [m^2/dm^3]	*R* [-]	UMFI × 10^3 [m^2/dm^3]	*R* [-]	UMFI × 10^3 [m^2/dm^3]	*R* [-]	UMFI × 10^3 [m^2/dm^3]	*R* [-]
7	0	0.5	2.716 ± 0.058	0.9980	2.235 ± 0.080	0.9943	2.462 ± 0.070	0.9964	1.823 ± 0.065	0.9955
7	100	0.5	2.808 ± 0.065	0.9995	2.283 ± 0.057	0.9986	2.529 ± 0.056	0.9994	2.523 ± 0.080	0.9991
7	200	0.5	2.060 ± 0.052	0.9972	1.751 ± 0.068	0.9934	1.898 ± 0.061	0.9955	0.667 ± 0.016	0.9945
5	0	0.5	2.989 ± 0.052	0.9987	2.387 ± 0.087	0.9942	2.668 ± 0.072	0.9968	2.345 ± 0.075	0.9956
9	0	0.5	0.697 ± 0.014	0.9984	0.657 ± 0.016	0.9977	0.677 ± 0.015	0.9981	2.402 ± 0.056	0.9979
7	0	0.1	1.645 ± 0.015	0.9996	1.451 ± 0.023	0.9989	1.544 ± 0.018	0.9994	1.496 ± 0.021	0.9992
7	0	0.9	1.849 ± 0.039	0.9980	1.603 ± 0.054	0.9951	1.721 ± 0.047	0.9967	1.661 ± 0.050	0.9959

The exemplary diagram of dependences between permeate fluxes and V_s including confidence intervals determined for significance level (α) equal to 0.05 is shown in Fig. 1.

The well fit of regression lines to measuring points was observed what additionally was confirmed by high value of correlation coefficients. Small measurement uncertain-

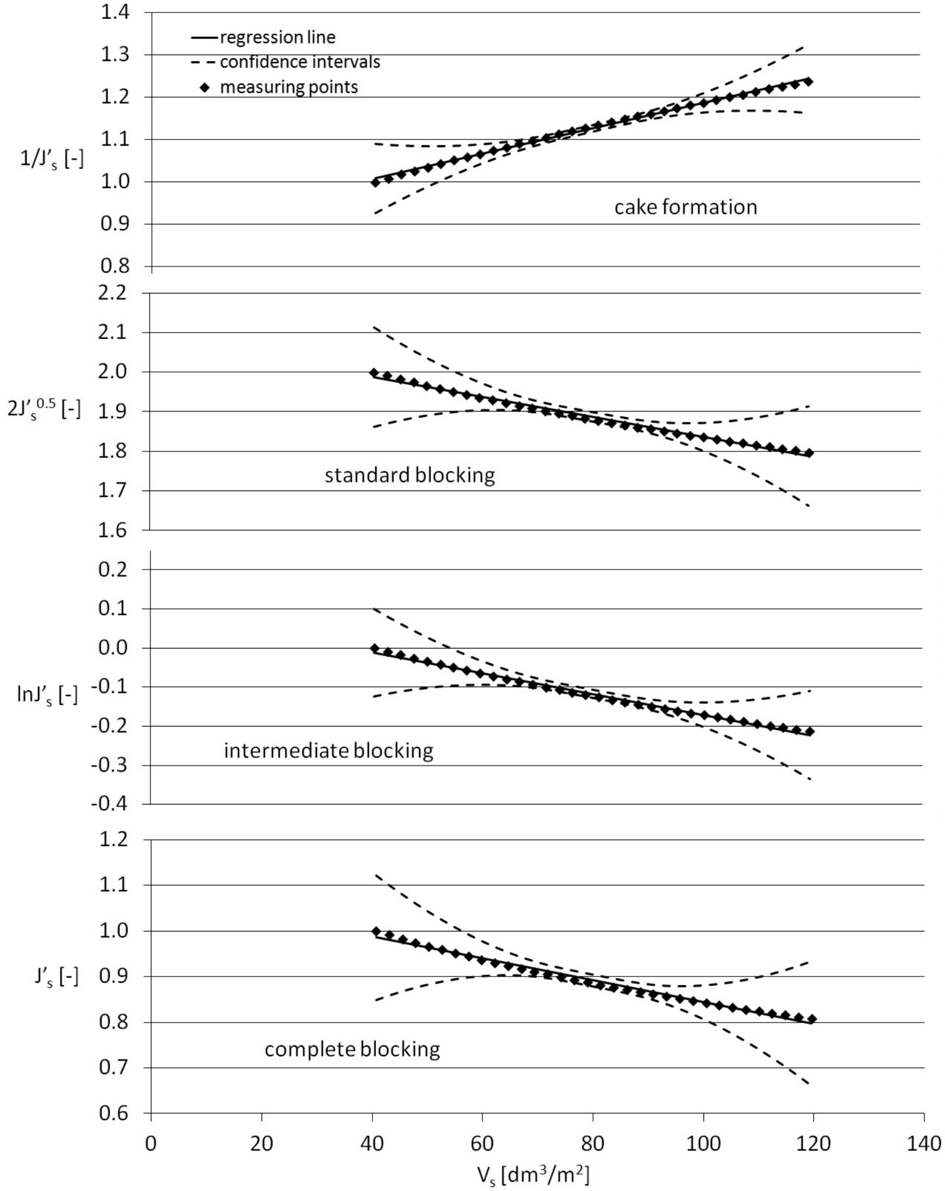

Fig. 1. The diagram of dependences between permeate fluxes and V_s (for water containing 100 mgCa/dm^3, pH = 7, $x_{H/D}$ = 0.5)

ties of UMFI were obtained in almost all of cases and did not exceed 4 %. All measuring points and regression lines were covered by the determined confidence interval *ie* interval to which estimated parameter value belongs with 95 % probability.

One of the main factors which influences on the fouling intensity is pH of the feed. The impact of pH on the intensity of fouling and its mechanisms occurred during filtrations is shown in Fig. 2.

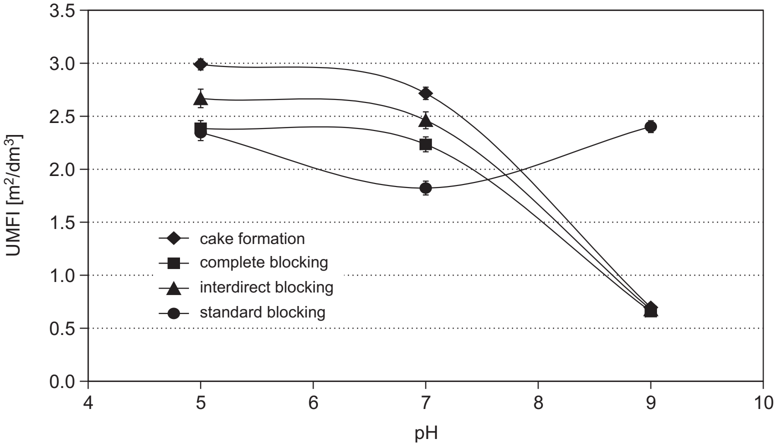

Fig. 2. Influence of pH on fouling (UMFI)

In case of membrane fouling the cake formation mechanism was the most significant, except from the filtration carried out under pH = 9. The mechanism in which pores contraction caused by the adsorption of organic substances takes place (*ie* standard blocking) had the negligible influence on fouling for pH range 5 to 7, while it was of the greatest importance in case of water pH equal to 9. The increase of alkalinity caused the increase of solubility of humic substances. It resulted in the increased number of molecules which were able to penetrate membranes pores and adsorb on their surface. For other fouling mechanisms *ie* cake formation, complete blocking and intermediate blocking the increase of pH caused the decrease of fouling intensity, which also could be explained by the change of solubility of organic substance in water. In feeds of alkaline character the similar influence of fouling mechanisms dominant in acidic waters (*ie* complete blocking, intermediate blocking and cake formation) was observed.

Simultaneously, with the decrease of fouling intensity the decrease of values of TOC (*Total Organic Carbon*) (Fig. 3), DOC (*Dissolved Organic Carbon*) and UV_{254} absorbance coefficients was observed. Additionally, values of retention coefficients indicated the better removal of humic substances than polysaccharides (dextranes) from the feed. PVDF (*Polyvinichidene fluoride*) membrane fouling was almost completely reversible (71–82 %). The higher pH of the feed the better recovery of the initial membrane capacity could be obtained, and the highest difference was noticed especially between pH = 5 or 7 and pH = 9 (11 % increase).

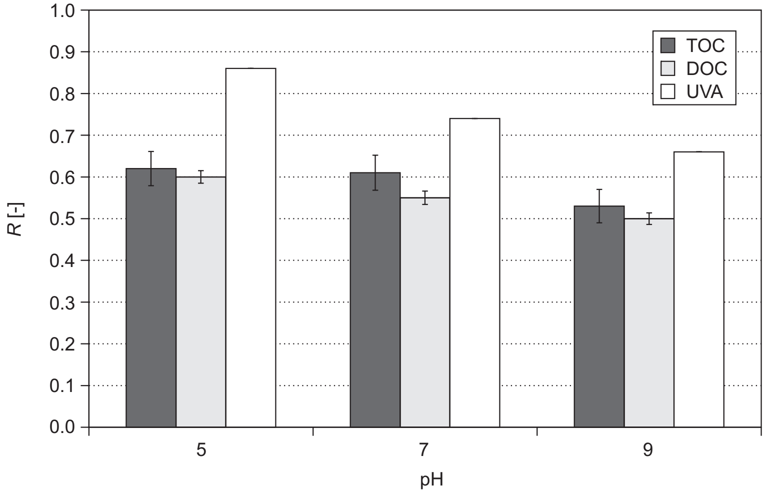

Fig. 3. Influence of pH on retention coefficients of organic matters

Calcium ions (high ionic strength) had also changed interactions in the membrane-feed system. The influence of calcium ions on the intensity of fouling is shown in Fig. 4 and on retention coefficients of organic impurities in Fig. 5. The increase of concentration of calcium ions resulted in the decrease of the fouling intensity. The appearance of 3 fouling mechanisms: cake formation, intermediate blocking and complete blocking was similar in case of various ionic strength waters as for various pH waters. However, the decrease of the fouling intensity was not as significant as when the feed pH was varied except from the index determined for the standard blocking mechanism. In case of the contraction of membrane pores the significant decrease of the UMFI index value with the increase of calcium ions concentration was observed (almost 3 times smaller UMFI for waters containing 200 mg/dm^3 of calcium in

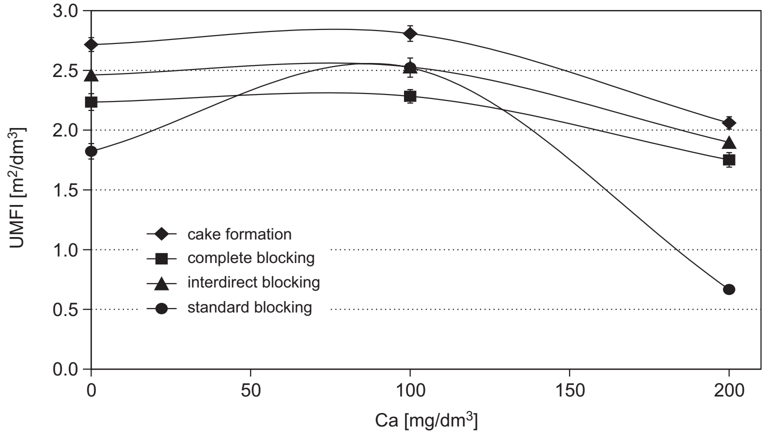

Fig. 4. Influence of calcium concentration on fouling

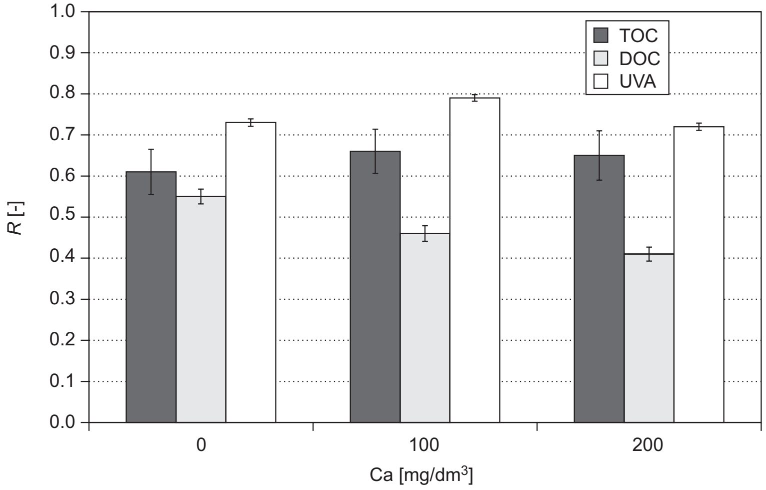

Fig. 5. Influence of calcium concentration on retention coefficients of organic metters

comparison with waters without calcium ions). In case of the feed of high ionic strength on the one hand organic substances form aggregates, while on the other hand the decrease of the apparent molecular weight is observed. According to that phenomenon, particles which firstly were adsorbed on membrane pores in case of high ionic strength were easily transported through the membrane or precipitated on the filtration cake formed by aggregates.

Calcium ions had a greatest influence on the removal of organic impurities indicated as DOC. The higher ionic strength in the feed the lower retention coefficients of DOC was observed. In the presence of calcium ions the retention of TOC increased negligibly. It can be explained by the aggregation of organic particles caused by the high ionic strength what resulted in the filtration cake formation. The increased calcium ions concentration caused also the more reversible form of fouling. The recovery of water flux increased more than 30 % in case of the feed containing 200 mgCa/dm^3 (the recovery degree exceeded 100 % what can be explained by the change of properties of membrane material caused by adsorption of organic and inorganic impurities) in comparison with the feed in which calcium ions were absent.

SUVA$_{254}$ index was used to determine the qualitative composition of natural water. The value of SUVA$_{254}$ ≥ 4 m^2/gC is characteristic for water which contains significant amount of hydrophobic, aromatic and high-molecular weight organic substances. The value of SUVA$_{254}$ ≤ 2 m^2/gC indicates that water contains mainly non-humic, hydrophilic, low-molecular weight substances. The mixture of hydrophilic and hydrophobic, low- and high-molecular weight substances is present in water with SUVA$_{254}$ value in the range 2–4 m^2/gC [9]. The influence of organic substances composition on fouling is shown in Fig. 6.

The parabolic dependence of UMFI indexes on SUVA was observed. The intensity of fouling during the filtration of feed waters containing mainly polysaccharides or

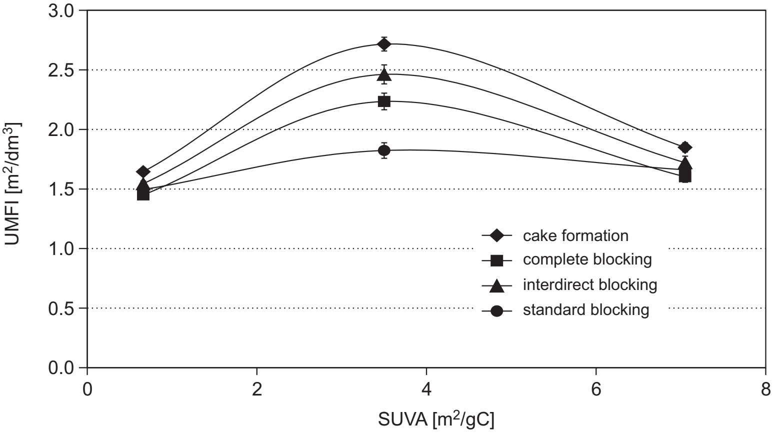

Fig. 6. Influence of SUVA on fouling (UMFI)

mainly humic compounds was insignificant and similar in both cases, while during the filtration of waters containing equal amounts of humic substances and dextranes the intensity of fouling was the greatest. In the second case the least reversible fouling was observed (*ca* 70 % recovery of the initial water flux). Similarly as in the study of the influence of pH and Ca on fouling the cake formation was the most significant mechanism.

The influence of SUVA on the degree of retention of organic substances defined by TOC, DOC and UVA is shown in Fig. 7. The decrease of UVA retention coefficient with the increase of SUVA was observed. However, the degree of UVA removal was the higher the smaller amount of substances able to absorb UV was present in the feed (the value of UVA for the water of the greatest SUVA indicator value was the order of magnitude higher than for the water of the smallest SUVA value). Both, retentions of

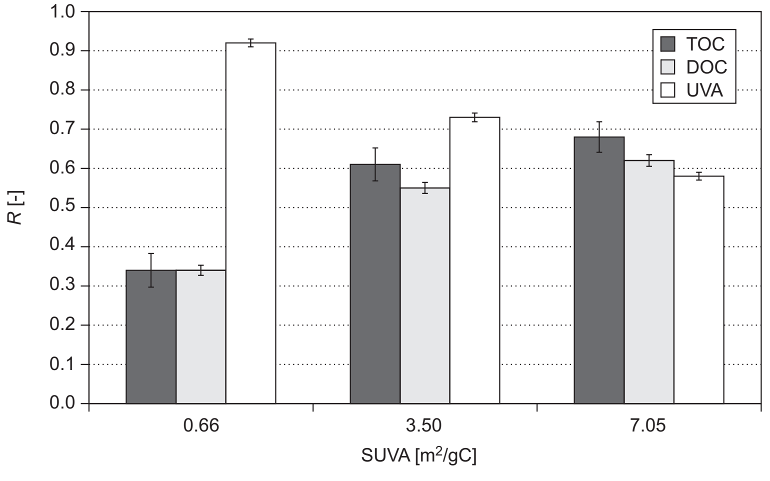

Fig. 7. Influence of SUVA on retention coefficients

TOC and DOC were greater for the greater value of SUVA index. It showed that PVDF membrane removed humic substances more effectively than polysaccharides.

Conclusions

The performed study showed that:

1. for the pH range 5–7 the cake formation mechanism is the most significant in case of membrane fouling, next the intermediate and complete blocking, while for pH = 9 standard blocking is of the greatest importance,
2. the increase of ionic strength and pH cause the decrease of fouling intensity and increase of its reversibility,
3. the substances of properties between hydrophilic and hydrophobic cause greater PVDF membrane blocking in comparison with strictly hydrophilic or hydrophobic substances,
4. PVDF membrane removes humic substances more effectively than polysaccharides,
5. the best removal of organic substances with the use of PVDF membrane occurs in waters which characterize with high ionic strength, low pH and hydrophobic substances content,
6. among parameters like pH, ionic strength and SUVA the feed water pH has the greatest influence on pH.

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BADANIE WPŁYWU WŁAŚCIWOŚCI WODY NA INTENSYWNOŚĆ I MECHANIZM ZJAWISKA FOULINGU W PROCESIE ULTRAFILTRACJI

Zakład Chemii Środowiska i Procesów Membranowych, Instytut Inżynierii Wody i Ścieków,
Wydział Inżynierii Środowiska i Energetyki, Politechnika Śląska

Abstract: Alternatywną metodą oczyszczania i uzdatniania wody w stosunku do metod klasycznych są procesy membranowe, którym towarzyszy nieodłącznie zjawisko foulingu, związane z obniżeniem wydajności i z akumulacją substancji organicznej bądź nieorganicznej na powierzchni membrany. W artykule omówiono wyniki badań wpływu właściwości wód (pH, rodzaj substancji organicznej, siła jonowa) na intensywność foulingu, wyrażoną za pomocą jednostkowego indeksu foulingu UMFI (U*nified Membrane Fouling Index*) i na mechanizm zjawiska.

Słowa kluczowe: ultrafiltracja, NOM, fouling, pH, siła jonowa

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Iwona SKOCZKO[1]

EFFECTIVENESS OF THE OPERATION OF THE SEWAGE TREATMENT PLANT IN AUGUSTOW

SKUTECZNOŚĆ DZIAŁANIA OCZYSZCZALNI ŚCIEKÓW W AUGUSTOWIE

Abstract: Water is not a commercial product as any other, but rather a good that has to be protected, defended and treated as a legacy. (European Parliament Directive 2000/60/EC). The best method for protection of groundwater is its efficient using and purified sewage amount increasing.

Therefore, it is important to build the construction and modernization of wastewater treatment plants. The water law defines the criteria of cleaned sewages which flow into water and ground.

Augustow is located in the northern part of the Podlasie province on borders of The Augustow Forest, on the river Rospuda-Netta [3]. The river is the receiver set of cleaned sewage from local sewage treatment plants. Rospuda-Netta river central section runs through the area of the special protection of birds PLC 200002, and the outcome section – through the area of The Biebrzanski National Park and simultaneously through the area of PLC 200001 entering in part of NATURE 2000. This is the reason of special wastewater purification.

The aim of the study was checking, whether the sewage treatment plant supporting Augustow and nearest communes supply into the receiver (Netta river) enough cleaned sewage and whether parameters of cleaned wastewater are within in an allowed range through statement of environmental impact.

Keywords: sewage, wastewater treatment plant, pollution parameters

Introduction

The examinations were conducted in the sewage treatment plant in Augustow. Almost the entire community has water-pipe network. A distribution plumbing exists in Augustow. The net of a sanitary sewage system works by gravitational-pump system. The length of the main sanitary sewage system net in the city is 83 km [1]. One sewage treatment plant operates in the city. There is increased removing biogenes system. Its capacity reaches about 10000 m^3 per day. 22.5 thousand of the town population uses the water supply system (74 %), however from a sewer system 20.3 thousand (66.8 %) [2]. The city is under construction of local distribution gas system. To the sewage treatment

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[1] Department of the Technology in Engineering and the Environmental Protection, Bialystok Technical University, ul. Wiejska 45A, 15–351 Białystok, Poland, phone: +48 85 746 96 44, email: iskoczko@pb.edu.pl

plant flows urban sewage with little amount (of the 10 %) of industry sewage. Wastewater from not-canalized areas (about 47 m^3/d) is delivered by vacuum trucks.

The sewage treatment plant was built and started up in 1978 as mechanical-biological system, with preliminary receptacles, with chambers of active sludge at their high load, with secondary settler tank and the chamber of the sludge regeneration. In 1998 modernization of the sewage treatment plant consisting in the change of the mechanical part was finished (Fig. 1). The changes covered sieves, grit chamber and preparing the sewage treatment plant for removing compound of carbons, nitrogen and phosphorus partly on the biological and partly chemical path. An increased effectiveness of sewers cleaning allowed particularly to increase biogenic pollutant reduction. Existing objects were modernised in order to form denitrification and nitrification chamber and to carry devices out for the internal recirculation of sewers from the chamber nitrification to denitrification and for the outside recirculation of deposit from secondary tank into the denitrification chamber. A sedimentary part was also modernised and devices were installed for mechanical dehydrating deposit.

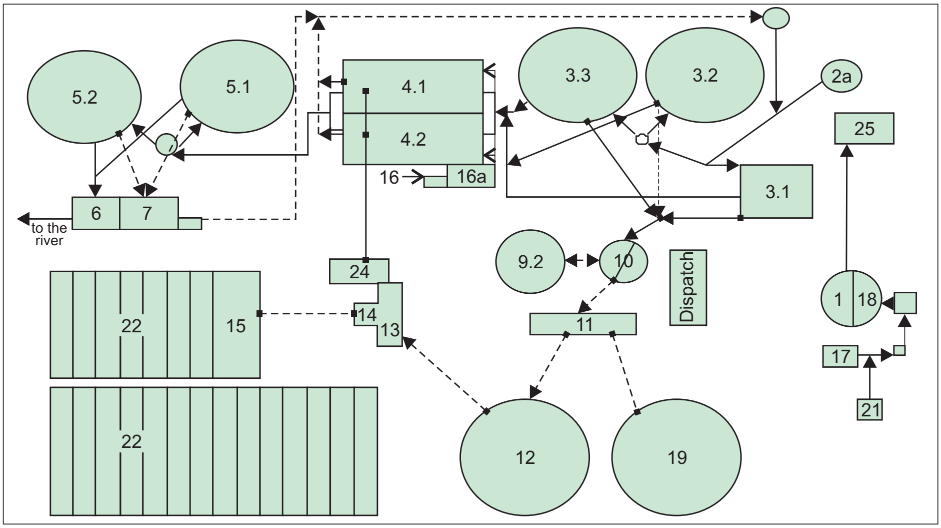

Fig. 1. The scheme of sewage treatment plant w Augustow: 1 – sewage pump house; 2a – vertical grit chamber; 3.1, 3.2, 3.3 – denitrification chambers; 4.1, 4.2 – nitrification chambers; 5.1, 5.2 – secondary settler's tanks; 6 – treated sewage pump house; 7 – sludge pump house; 9.2 – sludge disinfection; 10 – dual-purpose chamber; 11 – pump house; 12 – sludge stabilization chamber; 13, 14 – mechanical sludge drainage building; 15 – dehydrated sludge dump; 16 – PIX tank; 16a – PIX pump; 17 – septic tank; 18 – sewage pumping station; 19 – sludge tank; 21 – car washing station; 22 – sludge bed; 24 – air pomp building; 25 – sieves builing

Methodology of examinations

Samples of untreated and cleaned wastewater in the municipal sewage treatment plant in Augustow were being inspected. They were taken once a month, most often at the beginning of every month. The research period covered years: from January 2003 up to December 2008. Untreated sewage samples were picked up from primery settler tank and cleaned sewers from the channel carrying wastewater to the receiver.

In untreated and cleaned sewage were being marked the following pollutants parameters: suspension, *chemical oxygen demand* (COD), *biochemical oxygen demand* (BOD), general nitrogen, ammonium nitrogen, phosphates and general phosphorus. Obtained research findings constitute the arithmetic mean from three conducted parallel measurements.

Obtained research findings

BOD values in untreated sewers were levelled in the period of conducted examinations. The smallest BOD value was observed for sewers picked up in 2008 in the month October, and the biggest in September of 2004 (Fig. 2). BOD values for cleaned sewers were moved close in individual years, but it is possible to observe differences depending on the date of picking up sewers. Cleaned sewers taken since January by April and since the October by December were characterized with higher value of this indicator of about 8 mg/dm^3. Sewers picked up since May by September have had a little bit lower BOD value of about 5 mg/dm^3. Therefore, the degree of removing organic compounds being characterized by a BOD value was developed on the high, close the 100 %. Considerable differences in BOD values were not stated between individual years. It is possible to notice monthly analogies, when it appears increased BOD amount in sewers knocked off to the receiver. It was observed, that change of this parameter about 1.5 mgO$_2$/dm^3 appeared in the October 2006, 2008, took turns in May 2007 about 2 mgO$_2$/dm^3, and in the October about 1 mgO$_2$/dm^3. The norm according to statement of environmental impact takes out 15 mgO$_2$/dm^3 and was not crossed, because the greatest BOD value in sewers inserted into the receiver took out 8 mgO$_2$/dm^3 in March 2003.

The COD indicator of untreated sewers was diversified to a little extent depending on years of conducted examinations, as well as individual months what Figure 3 shows. It developed in the majority on the level of 500–800 mgO$_2$/dm^3. The highest crossing 1000 mg/dm^3 was for sewers from 2003 picked up since March by July, and the smallest for sewers from October 2008. The value of this indicator for cleaned sewers was diversified in years of conducted examinations. The high value was noticed in sewers picked up in 2003 and it was about 50–80 mg/dm^3. Peculiarly it was high for sewers picked up in the month January and July. From 2006 an effectiveness of cleaned sewers improved and COD values did not cross 30 mg/dm^3. The value of this indicator was not exceeded with regard to the established norm in statement of environmental impact – 125 mgO$_2$/dm^3. The step of cleaning of organic compounds being characterized by a COD value developed on the high, close the 100 %.

The amount of suspension (Fig. 2) in untreated sewers underwent fluctuations by 200–500 mgSiO$_2$/dm^3. Higher values of this indicator appeared in sewers picked up since June by September, lower in remaining months. Amount of suspension in sewers knocked off cleaned with regard to the norm from statement of environmental impact –

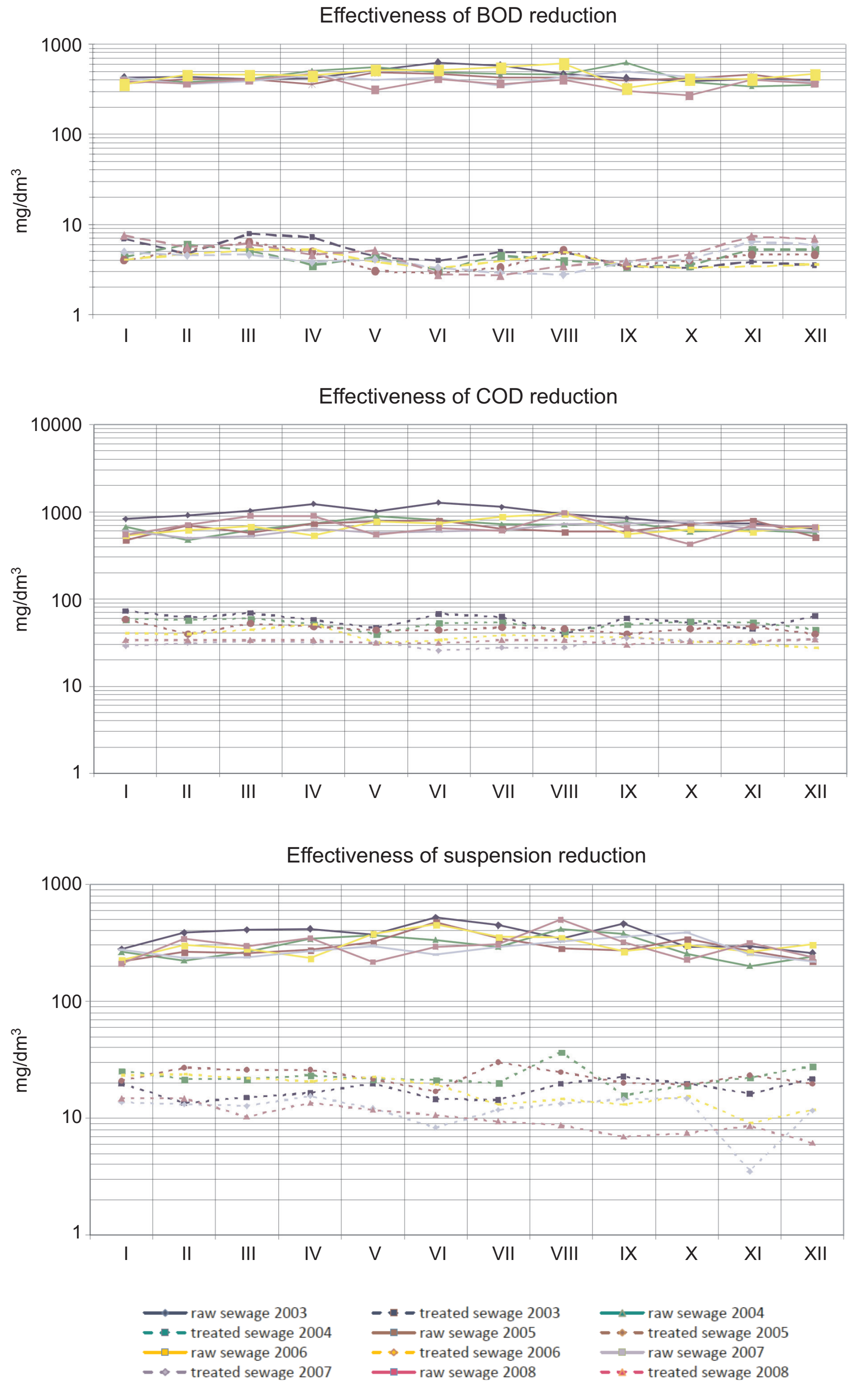

Fig. 2. BOD, COD and and suspensions values in strict and cleaned sewers

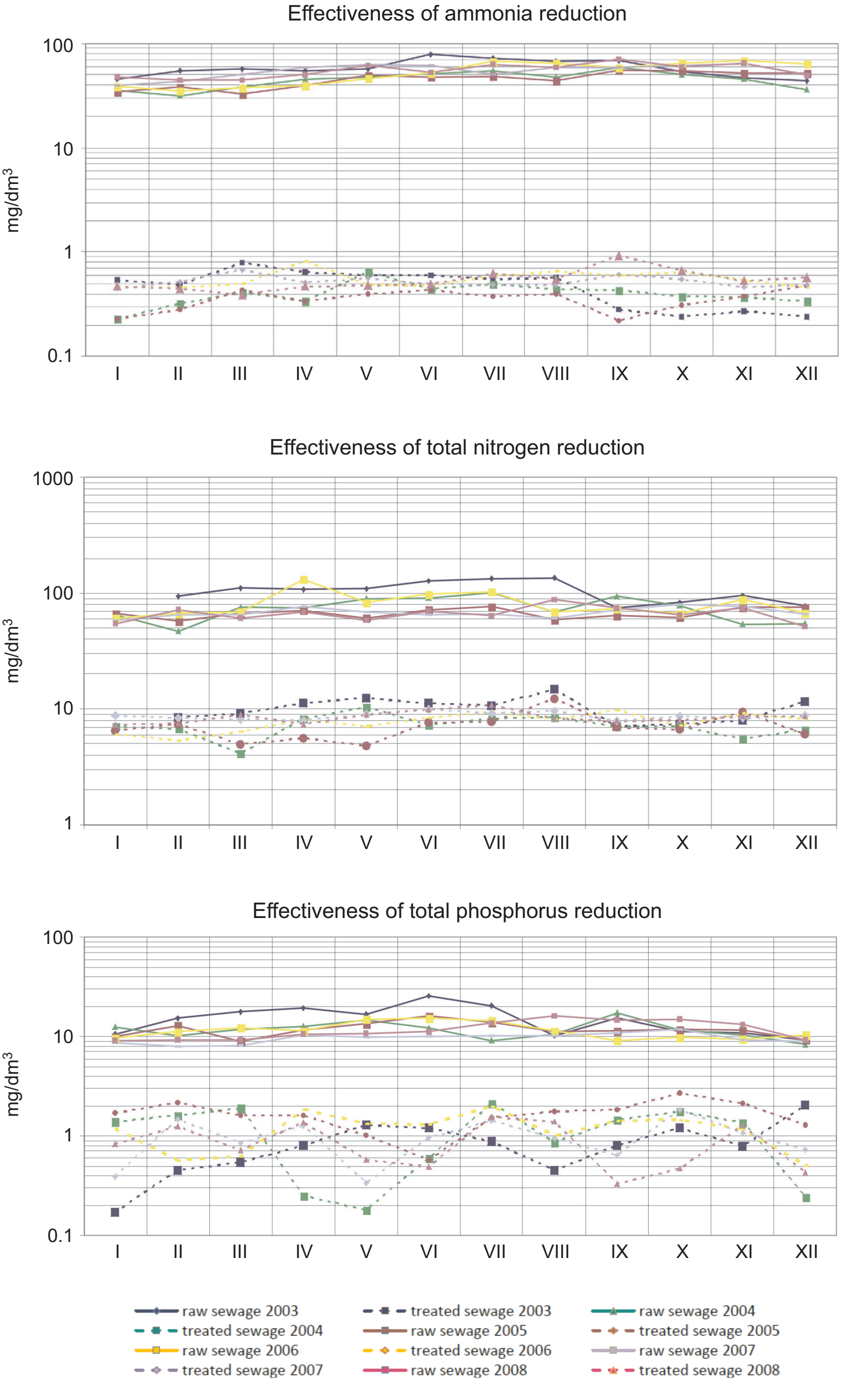

Fig. 3. Concentrations of compounds biogenic in strict and cleaned sewers

35 $mgSiO_2/dm^3$ was crossed in August 2004 – it was a sudden increase, because in previous months of this year the amount of suspension developed almost on the same level – 22 $mgSiO_2/dm^3$. The analogous big growth came in sewers picked up a year later, but it did not cross 35 $mgSiO_2/dm^3$ acceptable in statement of environmental impact. In 2003 the amount of suspension kept at a steady level between 14–22 $mgSiO_2/dm^3$. A fall in amounts of general suspension in sewers led to the receiver took place from July 2006 from about 20 $mgSiO_2/dm^3$ up to about 15 $mgSiO_2/dm^3$ and less in next months and years. The smallest amount of general suspension was observed in sewers picked up in October 2008.

The value of ammonium nitrogen and general nitrogen fluctuations was portrayed in years of conducted examinations (Fig. 3). Both indicators depict one group of pollutants and should be considered simultaneously. The content of general nitrogen in untreated sewage was moved close in all years, however the highest crossing was noticed in 2003 since March by August (about 100 mgN/dm^3), in remaining months there took place a distinct fall in the content of nitrogen. The lowest contents of this indicator appeared in sewers picked up in February 2004. Diversified concentrations of ammonium nitrogen in untreated sewage divided every year of examinations in three parts. This indicator had the lowest values in months since December up to March, the highest from April by September, next then again decreasing since October by November. The greatest concentration was noticed in June 2003, the lowest in February both March 2004 and 2005. From 2007 there was observed a stabilization of the ammonium and general concentration of nitrogen.

In spring-summer months general nitrogen was removed in the worst way. Its concentration in cleaned sewage knocked off to the river only in August achieved 2003 acceptable maximum in statement of environmental impact – of 15 mg/dm^3. In sewers from remaining years this norm was not exceeded. This indicator surrendered considerable for fluctuations in cleaned sewers: by 4–5 mgN/dm^3 in early-spring months in 2004–2005 years to 13–15 in summer months of 2003. In years 2003–2005 there was observed swings of amounts of general nitrogen in sewers knocked off to the receiver in individual months, however in next years this tendency underwent the levelling out and fluctuated between 7–10 $mg\ N/dm^3$.

Concentrations of ammonium nitrogen in purified sewage in summer periods underwent the stabilization, however their fluctuations in every year were observed within the limits of 0.4–0.6 $mgNH_4/dm^3$. Amplitude tarsometatarsuses of the fluctuations appeared since September by April. The greatest was determined in September 2008 – concentration about 1 $mgNH_4/dm^3$. The lowest value of this indicator in cleaned sewers was in January 2004 and 2008 – about 0.2 $mgNH_4/dm^3$. On the basis of concentrations was calculated the removing ammonium nitrogen degree of sewage and it is shown on graphs. It took out over the 98 %.

In Figure 3 there were described values of general phosphorus concentrations. In untreated sewers concentrations of this indicator was levelled in the entire research period. The exception constitutes 2003, when in June a high concentration was noticed about 12 mgP/dm^3. In sewers from remaining years values of this indicator fluctuated from 8 mgP/dm^3 in January and March 2007 to 10 mgP/dm^3 in June, August and

September in 2006 and 2008. Phosphorus is a biogene surrendering in the course of conducted research works for the greatest hesitations in cleaned sewers. In 2005 the maximum concentration, agreeable from water law (2 mgP/dm^3), was crossed in February and October, slight crossed in August 2004 and December 2003, and resembled to the maximum value in August 2006. The lowest values about 0.15 mgP/dm^3 was noticed in sewers picked up in January 2003 and May 2004.

Discussion

The effectiveness of cleaning sewage in existing objects of the sewage treatment plant is the subject of the research of many scientists from the entire country [4–6]. In the Podlasie province were conducted inspections of untreated sewers reaching to the sewage treatment plant and cleaned sewers by Dabrowski [7], Boruszko [8], Dzienis [9], Wawrentowicz [10], Skoczko [11] and others. According to the literature, applied biological system is enjoying considerable influence to the effectiveness of cleaned sewers in the given sewage treatment plant. Shore-out to zones: anoxic, anaerobic and aerobic is important too. For removing phosphorus the significance has an application of appropriate coagulant. Its correct acting is also affecting the operation of the part of the mechanical sewage treatment plant [7] and work of secondary chamber [9].

The situation of Augustow and his special character of the holiday town have a significant influence to the amount of delivered sewage, peculiarly in summer months. Augustow is a recognised spa and tourist city what in the holiday season is pursuing residents for doubling the number. It is transferred into the growth of the amount of sewage in July and August. Literature inform that the composition of untreated sewage depends from industrializing the region of both sewage amount and quality [7, 8]. This statement has a distinct reflection in case of Augustow. On all described graphs it is possible to notice an increase of the number of pollutants indicators in untreated sewers in summer months, when a number of sewers delivered to the sewage treatment plant is rising with sanitation means of transporting. This growth has an influence on cleaned sewers quality. Only phosphorus concentrations is independent of these hesitations, because according to literature [7] the effectiveness of dismissing its depends on the optimum selected dose of coagulant and on correct time of keeping sewers in the secondary chamber.

Analysing obtained research results of untreated and cleaned sewers in years 2003–2008, it is possible to state that satisfying effects of removing individual compounds from sewage were achieved in the sewage treatment plant in Augustow. It has, of course, more distant influence on the state of water in the receiver. The research results were comparing with permissible norms from statement of environmental impact [1] and with the permissible highest values of indicators from the Regulation of the Environment Secretary from day 8th July 2004. "In the case of conditions which should be met by sewage inserting to water or to the soil and in the case of substances which are particularly harmful to the environment of water" [12] it is possible to state, that permissible values of pollutants indicators in sewage carried to the receiver in statement of environmental impact are lower. On the other hand the concentration of general phosphorus was exceeded in some months, in comparing with requirements statement of environmental impact. However it towards the regulation did not cross the maximum size of 3.0 mg P/dm^3 which is in enclosure no. 1 to this regulation.

Conclusions

1. Cleaned sewage knocked off has not an influence on the class of receiver water which is staying the COD on the level of the III class largely disqualified by the indicator.
2. Flowing sewage to the receiver occasionally exceeds norms. Pollution of general phosphorus concerns the exceeding what does not agree with values allowed by the Regulation of the Environment Secretary from 8th July 2004.
3. In the period of conducting research worsening the quality of cleaned sewers was not observed, however the distinct growth of inspected indicators concentrations were ranked as well as large amounts of sewers delivered in the summer season.
4. Rainwater both from the city of Augustow and nearby towns are affecting the quality of water in the receiver – the Netta River.

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SKUTECZNOŚĆ DZIAŁANIA OCZYSZCZALNI ŚCIEKÓW W AUGUSTOWIE

Katedra Technologii w Inżynierii i Ochronie Środowiska
Politechnika Białostocka

Abstrakt: Woda nie jest produktem komercyjnym, takim jak każdy inny, lecz raczej dobrem, które musi być chronione, bronione i traktowane jak dziedzictwo. (Parlament Europejski i Rady Unii Europejskiej: „Ustanowienie ram dla działalności Wspólnoty w dziedzinie polityki wodnej”, Dyrektywa 2000/60/EC) Najlepszą metodą służącą do ochrony wód jest jej oszczędne używanie oraz zwiększenie ilości poprzez oczyszczanie ścieków, czy innego rodzaju zanieczyszczonych wód powierzchniowych. Z tego względu tak ważna jest budowa i rozbudowa oczyszczalni ścieków. Kryteria, jakim muszą odpowiadać ścieki oczyszczone, które odprowadzane są do wód i ziemi, określa prawo wodne.

Augustów położony jest w północnej części województwa podlaskiego na obrzeżach Puszczy Augustowskiej, nad rzeką Nettą, będącą jednocześnie odbiornikiem ścieków oczyszczonych lokalnej oczyszczalni. Środkowy odcinek Rospudy-Netty przebiega przez obszar specjalnej ochrony ptaków PLC 200002 „Puszcza Augustowska”, a odcinek ujściowy – przez obszar Biebrzańskiego Parku Narodowego i jednocześnie obszar PLC 200001 „Dolina Biebrzy”, wchodzące w skład Europejskiej Sieci Ekologicznej NATURA 2000.

Celem prowadzonych prac badawczych było zatem sprawdzenie, czy oczyszczalnia ścieków Augustów obsługująca teren miasta i gminy wprowadza do odbiornika ścieków (rzeki Netty) ścieki wystarczająco oczyszczone i czy uzyskane parametry ścieków oczyszczonych mieszczą się w zakresie dopuszczonym przez operat wodno-prawny.

Słowa kluczowe: ścieki, oczyszczalnia ścieków w Augustowie, wskaźniki zanieczyszczeń

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Beata KOWARSKA[1], Jerzy BARON[2],
Witold ŻUKOWSKI[2], Jadwiga ZABAGŁO[2]
and Małgorzata OLEK[1]

LOW-EMISSION COMBUSTION IN A FLUIDISED BED REACTOR

SPALANIE NISKOEMISYJNE W REAKTORZE ZE ZŁOŻEM FLUIDALNYM

Abstract: Regardless of the type of fuel and organization of the combustion process, usage of air as an oxidizer in this process is a source of nitrogen oxides emission. Significant increase in the emission occurs when fuel is itself a source of nitrogen. The nitrogen oxides formed in combustion processes, conducted in industrial processes, in power industry as well as in households pose a serious threat to the environment and human health when released to the atmosphere. Apart from solid fossil fuels, solid biomass is being increasingly used for energy purposes. However, it does contain significant amounts of nitrogen, usually exceeding the amount of nitrogen found in coal, in the form of organic bases and amino acids. Combustion of biomass, on the one hand, could lead to significant reduction in the growth of CO_2 emission into the atmosphere, however; on the other hand it could become a significant factor in the increase in global emission of nitrogen oxides. Use of techniques and technologies that protect the atmosphere from an inflow of additional stream of nitrogen oxides would, therefore, seem inevitable. Besides methods involving chemical reduction of NO_x in flue gases in isolation from the area where is the source of flue gases, methods for reducing amount of nitrogen oxides in the exhaust fumes carried in the combustion zone, are also known and applied. This paper presents results of experimental studies in which two-zone combustion in bubble fluidised bed reactor was applied in aim to reduce of NO concentration in flue gases

Keywords: low-emission combustion, fluidised bed combustion, nitrogen oxides reduction methods

Formation of nitrogen oxides in combustion processes

Nitric oxide can be produced in the process of combustion of fuel, from atmospheric and fuel nitrogen, through a number of different mechanisms. During the complex

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[1] Faculty of Environmental Engineering, Krakow University of Technology, ul. Warszawska 24, 31–155 Kraków, Poland, phone: +48 12 628 27 67, 628 25 92, email: beatak@chemia.pk.edu.pl, mmt.olek@gmail.com

[2] Faculty of Chemical Engineering and Technology, Krakow University of Technology, ul. Warszawska 24, 31–155 Kraków, Poland, phone: +48 12 628 27 09, 628 27 66, 628 27 97, email: baron@pk.edu.pl, pczukows@pk.edu.pl, jagakaz@interia.pl

processes leading to generation of NO, a number of radicals are produced and, depending on thermodynamic and stoichiometric conditions, the number of these radicals can be regulated. This makes it possible to modify the course of the entire process of production of NO, leading, for example, to reduction in the rate of its formation.

The following reactions describe the thermal mechanism of formation of NO (Zeldovich mechanism) [1]:

$$O^{\bullet} + N_2 \rightarrow NO + N^{\bullet}$$
$$N^{\bullet} + O_2 \rightarrow NO + O^{\bullet}$$
$$N^{\bullet} + OH^{\bullet} \rightarrow NO + H^{\bullet}$$

According to this mechanism, the thermal dissociation of oxygen and nitrogen molecules in the air is the start of processes leading to the formation of NO. The high energy of formation of these bonds, especially in the nitrogen molecule, makes formation of NO possible through this mechanism only under high temperatures. In practice, during combustion process in a fluidised bed reactor, where the temperature is much lower than 1400 ^{o}C, it is possible to omit the participation of NO formed in accordance with the thermal mechanism in practically all produced nitrogen oxides [2].

Combustion of hydrocarbon fuels at temperature lower than 1000 ^{o}C may lead to formation of relatively high concentrations of NO in the flue gases [3]. Fenimore has proposed a mechanism of formation of NO under such conditions, a mechanism called "prompt", of which following reactions are crucial [4–6]:

$$CH^{\bullet} + N_2 \rightarrow HCN + N^{\bullet}$$
$$CH_2 + N_2 \rightarrow HCN + NH^{\bullet}$$
$$HCN + O^{\bullet} \rightarrow NCO^{\bullet} + H^{\bullet}$$
$$NCO^{\bullet} + O^{\bullet} \rightarrow NO + CO$$

NCO and NH radicals in reaction with NO are the source of N_2O – an oxide with several times higher absorption of infrared radiation, a key greenhouse gas property, than CO_2.

At temperatures below 1200 ^{o}C, in the presence of O radical, not only N_2O could be produced, but also NO in the subsequent reaction, which is consistent with reaction mechanism proposed by Malte and Pratt [7]:

$$N_2 + O^{\bullet} + M \rightarrow N_2O + M$$
$$N_2O + O^{\bullet} \rightarrow 2NO$$

The formation of NO from nitrogen bound in the fuel is a process that requires much lower energy input. Nitrogen – usually tied up in organic matter in cyclic or amine compounds – is more susceptible to reactions at elevated temperatures. It appears transiently in the processes of combustion in hydrogen cyanide, radicals CN, HNO, and

NH_i. Key reactions leading to the formation of NO are described using the following reaction equations [8–10]:

$$
\begin{aligned}
&HCN + M \rightarrow CN^{\bullet} + H^{\bullet} + M\\
&HCN + H^{\bullet} \rightarrow CN^{\bullet} + H_2\\
&CN^{\bullet} + OH^{\bullet} \rightarrow HCO^{\bullet} + N^{\bullet}\\
&CN^{\bullet} + O^{\bullet} \rightarrow CO + N^{\bullet}\\
&CN^{\bullet} + O_2 \rightarrow NCO^{\bullet} + O^{\bullet}\\
&NCO^{\bullet} + O^{\bullet} \rightarrow NO + CO\\
&NH^{\bullet} + O^{\bullet} \rightarrow NO + H^{\bullet}\\
&NH^{\bullet} + OH^{\bullet} \rightarrow HNO^{\bullet} + H^{\bullet}\\
&NH_2^{\bullet} + O^{\bullet} \rightarrow HNO^{\bullet} + H^{\bullet}\\
&HNO^{\bullet} + H^{\bullet} \rightarrow NO + H_2\\
&HNO^{\bullet} + OH^{\bullet} \rightarrow NO + H_2O\\
&HNO^{\bullet} + O^{\bullet} \rightarrow NO + OH^{\bullet}
\end{aligned}
$$

It is characteristic that OH radical which plays a very important role in the process of oxidation of carbon bounds in organic matter into CO also plays a very important role in oxidation, occurred in the combustion processes, nitrogen compounds to nitric oxide.

Methods of reduction of NO in the flue gases

NO formed in the combustion processes should be removed from flue gases before their discharge into the atmosphere. This, in particular, applies to combustion of biomass or fossil fuels with high nitrogen content. The primary methods of reduction of NO are implemented in such a way that reduction process takes place in a reactor in which combustion occurs. In industrial practice, these primary methods include *selective non-catalytic reduction* (SNCR) and reburning. The process of reduction of NO in the secondary methods is conducted in separate reactors (installations), and more frequently *selective catalytic reduction* SCR is used.

SNCR method consists in injecting stoichiometrically selected amount of ammonia or urea to the combustion zone. These substances undergo changes, as a result of which NH_i radicals are formed and these in turn react with NO reducing it to N_2. The process with use of ammonia is carried out at the temperature range 770–1000 ^{o}C. In the case of using urea, the first stage of the process (decomposition of urea) takes place in the temperature range 300–620 ^{o}C. The key reactions determining the mechanism leading to the reduction of nitric oxide in selective non-catalytic NO reduction method are shown below: [11, 12]:

$$
\begin{aligned}
&NH_3 + OH^{\bullet} \rightarrow NH_2^{\bullet} + H_2O\\
&NH_3 + O^{\bullet} \rightarrow NH_2^{\bullet} + OH^{\bullet}\\
&CO(NH_2)_2 \rightarrow NH_3 + HNCO\\
&NH_2^{\bullet} + NO \rightarrow N_2 + H_2O
\end{aligned}
$$

$$NH_2^{\bullet} + NO \rightarrow NNH^{\bullet} + OH^{\bullet}$$
$$NNH^{\bullet} + NO \rightarrow N_2 + HNOB^{\bullet}$$

In this method maintaining of appropriate temperature is significant, because at temperatures above 1093 ^{o}C there is acceleration of the rate of oxidation of ammonia as follows:

$$4NH_3 + 5O_2 \rightarrow 4NO + 6\ H_2O$$

resulting in production of significant amounts of NO. It is possible to achieve reduction of NO by about 70 % through regulation of the amount of added ammonia [12, 13] and temperature range. This so-called "temperature window" in SNCR technology may be expanded by introducing into the reaction zone, in addition to ammonia, compounds such as: $CH_{4,}$ $C_2H_{4,}$ C_2H_2, C_2,H_6, H_2O_2, CH_3OH, CH_3NH_2 [11, 14]. However, addition of these compounds increases emission of NO_2, N_2O, CO and HCN and reduces excessive reaction of NH_3, which seems to constitute a serious limitation of their use. In practice, urea is often used in SNCR method, because storage of large quantities of pressurized ammonia is technically cumbersome and risky, due to the fact that ammonia forms an explosive mixture with air.

SCR [15] is carried out after the combustion chamber, where reactions take place under in the presence of appropriately selected catalysts, often ammonia is the reducing reagent used. Use of catalyst reduces activation energy for reactions leading to N_2. The following reaction equations describe reduction process taking place on a platinum catalyst:

$$4NH_3 + 4NO + O_2 \rightarrow 4N_2 + 6H_2O$$
$$4NH_3 + 2NO_2 + O_2 \rightarrow 3N_2 + 6H_2O$$
$$4NH_3 + 6NO \rightarrow 5N_2 + 6H_2O$$
$$8NH_3 + 6NO_2 \rightarrow 7N_2 + 12H_2O$$

In such a system there is a risk of adverse reaction leading to N_2O taking place. The following catalysts are used in SCR: platinum, tungsten-vanadium catalysts supported on TiO_2, ZrO_2, SiO_2, Al_2O_3, and zeolite carriers [15, 16].

Introduction of additional fuel in zone above the fluidised bed, which means creation of second combustion zone, is among the major early methods of reducing NO. The architects of this method, Wendt et al [17], called it reburning. Its effectiveness is based on a process that can be describe by the net equation:

$$2NO + C_3H_8 + 4O_2 \rightarrow N_2 + 3CO_2 + 4H_2O$$

Babcock & Wilcox Company in the USA [18] in the early 90s unveiled a technology on an industrial scale – a coal-burning reactor with a capacity of 100 MW. They obtained a degree of reduction of nitrogen oxide equal to approximately 50 %. Ever since, due to its advantages, reburning has been widely used [19–22] especially in power industry. In the first applications of reburning process coal was used as additional (secondary) fuel, it was at the same time fuel in the first combustion zone, [18, 19]. It is still practiced to this day, because multiple power plant installations as well as installations from other industries all over the world using coal as fuel. These installations are a major source of nitrogen oxides emission. Many of them do not have technical solutions, which would allow for simultaneous combustion of two fuels – solid as the main fuel and gas as reburning fuel. For these reasons, there are ongoing researches on reburning process, where coal is the source of fuel [19]. If the air fuel ratio in the range 0.7–1.1 is maintained in the case where coal is the fuel, a 60–70 % reduction of NO_x is achieved. Gaseous hydrocarbons are second reburning fuel in use [20, 23, 24]. Recent studies [20] show that using such reburning fuel, with appropriately calculate time in which the reactants are in the combustion chamber in the 350 MW installation, it was possible to obtain conversion of NO at a level exceeding 60 %. In recent years there have been a lot of information on use of biomass or other waste, such as meat waste or tires, as reburning fuel [14, 21, 25, 26]. Maintaining appropriate process, parameters, conversion of NO into N_2 at a level exceeding 80%, was achieved [21, 26].

The purpose of this work is to explore ways of using reburning as a new process solution in a bubble fluidised bed reactor. So far, combustion processes have been carried out in such one-zone reactors, however, combustion of biomass resulted in exceeding NO_x emission limits. This lead to studies in the direction of search of effective means of reducing produced nitrogen oxides. Simple design solutions led to injection of fuel gas in the area above the fluidised bed and creation of a second combustion zone. Biomass combustion was simulated during experiments on combustion of propane, to which a steady stream of nitric oxide was added to its mixer with air.

Material and methods

Combustion process was carried out in a fluidised bed reactor, in the shape of a cylinder, whose sidewall was a quartz tube with a diameter of 96 mm and height of 500 mm (Fig. 1). It was put on chrome-nickel perforated plate with a thickness of 1 mm constituting a distributor. The reactor was equipped with a temperature control system consisting of moving heat shield and cold air blower. Eight thermocouples mounted in the axis of the reactor, one above the other, at a distance of 115 mm to 180 mm above the distributor were used to measure the temperature, their distribution is shown in Fig. 1. The exhaust gases for chemical analysis were collected from zone above the fluidised bed by heated-probe and directed into a system of analyzers. The reactor was equipped with a movable reburning fuel dosage system, in the specified experiment it was placed 130 mm above the distributor. 300 g of sand of grain size 0.385–0.430 mm constituted a chemically inert bed. Evaluation of the process of combustion was accomplished through analysis of composition of flue gases and measurements of temperature in reburning zone. Two zone combustion of technical grade propane in the air was carried out in such a fluidised bed reactor, with the constant 40 $\%_{vol}$ air excess in the first combustion zone. During the experiments 500 ppm of NO was added to the fuel-air mixture. The experiment consisted of the following stages: cold fluidization of the bed, introducing a steady stream of NO to the bed, lighting up and heating reactor to

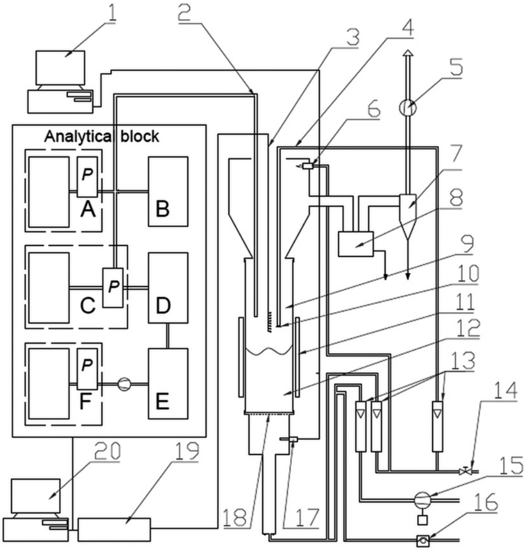

Fig. 1. Schematic representation of fluidised bed reactor: 1 – computer storing the pressure data, 2 – heated probe for sampling the flue gases, 3 – set of 8 thin thermocouples, 4 – reburning fuel's supply system, 5 – exhaust fan, 6 – pilot flame, 7 – cyclone, 8 – ash trap for coarser particles, 9 – second combustion zone, 10 – outflow of reburning fuel, 11 – movable radiation shield, 12 – bubbling fluidised bed, 13 – rotameters (from left: air and primary and secondary fuel), 14 – fuel supply valve, 15 – blower, for fluidising air, 16 – peristaltic pomp NO, 17 – pressure difference sensor, 18 – flat, perforated metal plate distributor, 19 – A/D converter for thermocouple signals; 20 – computer storing chemical analyses quantities and temperature.
Analytical block: A – O_2, CO, NO, NO_2, SO_2, CH_4, CO_2 analyser (MRU Vario Plus), B – total hydrocarbon analyser (JUM Model 3-200), C – O_2, CO, NO, NO_2, SO_2 analyser (ECOM SG Plus), D – CO_2 analyser (Madur), E – N_2O analyser (Horiba VA3000), F – O_2, CO, CO_2, SO_2, NO_x analyser (Horiba PG250), P – Peltier's cooler

a temperature of about 900 ^oC, switching on of flow of reburning fuel – propane – and start of process of two-zone combustion in the reactor, stepwise increasing amounts of reburning fuel from 0.006 dm^3/s to 0.015 dm^3/s. Results of the experiments are illustrated in Fig. 2.

Results and discussion

Temperature was kept constant at about 900 ^oC during the experiment. With the start of the two-zone combustion process in a fluidised bed reactor, the composition of flue gases changed (Fig. 2). As the stream of hydrocarbon fuel added to the reburning area increased the proportion of oxygen in that area decreased. When propane was added to the reburning zone, at a rate of 0.015 dm^3/s, oxygen concentration in the flue gases dropped to its lowest value, *ie* about 0.2 %. As the added jet of reburning fuel to the rare zone of fluidised bed was increased, there was a noted decrease in concentration of NO in the flue gas. Its lowest value – about 250 ppm – was registered at flow rate of

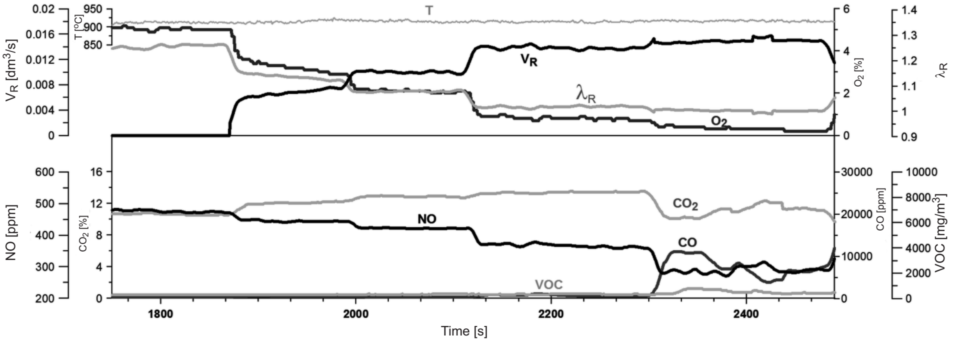

Fig. 2. Selected parameters of combustion process in fluidised bed and emissions of NO, VOC, CO_2 and CO in the experiment; (index R – in reburning area)

propane in the second combustion zone equal to 0.015 dm^3/s (Fig. 2). Concentration of CO_2 during the experiment gradually increased in proportion to the increase of reburning fuel stream. After exhausting of oxygen in reburning zone (air fuel ratio decreased below 1.00), there is a significant drop in concentration of CO_2 in the exhaust, accompanied by a sharp increase in concentration of CO to a value greater than 10000 ppm as well as increase in concentration of *volatile organic compounds* (VOC) to more than 400 mg/m^3. This result indicates the importance of maintaining the value of air excess coefficient close to 1 or greater than 1 (fuel mixture richer in oxygen) for proper carrying on of combined processes of combustion of biomass and reduction of NO concentration in the flue gases.

Conversion of NO reached a maximum value of 53% for air excess coefficient – λ_R equal to 1 (Fig. 3), flow volume of reburning fuel was then equal to 0.015 dm^3/s. By

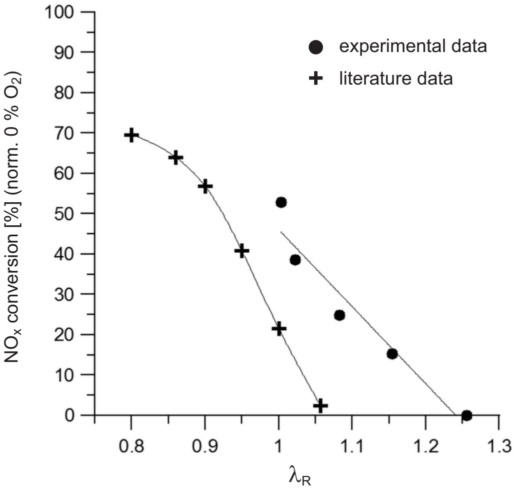

Fig. 3. Relationship between conversion of the nitrogen oxides to N_2 and air excess coefficient in reburning area (index R – in reburning area)

comparing conversion rates obtained in the experiments with literature data [27] (Fig. 3), we can see that achievement of specified level of reduction of NO in fluidised bed reactor as obtained for higher (environmentally safer) value of air excess coefficient. Using a fluidised bed reactor to carry out two zone combustion, it is possible to achieve conversion of NO higher than 50 % under air excess coefficient equal to 1 (Fig. 3). Using other reburning technologies the value of λ_R has to be reduced significantly below 1, involve the need to use more reburning fuel and results in higher percentage of CO and hydrocarbons in exhaust fumes, which must then be further burn in the last (third) combustion zone.

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SPALANIE NISKOEMISYJNE W REAKTORZE ZE ZŁOŻEM FLUIDALNYM

[1] Wydział Inżynierii Środowiska, [2] Wydział Inżynierii i Technologii Chemicznej
Politechnika Krakowska

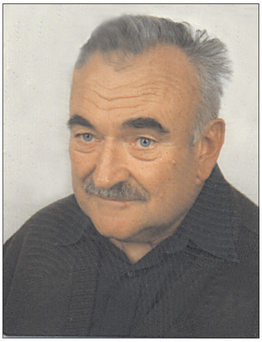
Abstrakt: Niezależnie od rodzaju paliwa oraz organizacji procesu spalania użycie powietrza jako nośnika utleniacza w tym procesie jest źródłem emisji tlenków azotu. Znaczny wzrost tej emisji następuje wtedy, gdy źródłem azotu jest samo paliwo. Tlenki azotu powstające w procesach spalania realizowanych zarówno w procesach przemysłowych, w energetyce zawodowej, jak i w gospodarstwach domowych, przedostając się do atmosfery, stanowią poważne zagrożenie dla środowiska naturalnego i zdrowia. Obok kopalnych paliw stałych w coraz większym stopniu wykorzystywana jest w celach energetycznych biomasa stała zarówno roślinna, jak i zwierzęca. Zwiera ona jednak w formie zasad organicznych i aminokwasów znaczące ilości azotu, zwykle przekraczając ilości spotykane w węglach energetycznych. Spalanie biomasy z jednej strony może prowadzić do istotnego ograniczenia wzrostu emisji CO_2 do atmosfery, z drugiej, może stać się istotnym czynnikiem wzrostu globalnej emisji tlenków azotu. Nieuniknione jest wobec powyższego stosowanie technik i technologii chroniących atmosferę przed dopływem dodatkowego strumienia tlenków azotu. Oprócz metod polegających na chemicznej redukcji zawartości NO_x w spalinach w oderwaniu od miejsca powstawania spalin, znane i stosowane są również metody zmniejszania ilości tych substancji w spalinach realizowane w strefie spalania. W niniejszej pracy zaprezentowano wyniki badań eksperymentalnych, w których do obniżenia stężenia NO w spalinach wykorzystano spalanie dwustrefowe w pęcherzowym reaktorze fluidyzacyjnym.

Słowa kluczowe: spalanie niskoemisyjne, spalenie w złożu fluidalnym, metody redukcji tlenków azotu

Varia

IN MEMORIAM

Wiesław SKORUPSKI (*1932–†1999)



In 2012, on the occasion of the eightieth birthday anniversary of Doctor Wiesław Skorupski, we remember a respected chemist, teacher and our dear colleague. When he passed away in 1999, soon after His death memories of those who knew and valued Him were published[1, 2, 3]. The memories depicted Him as a gifted and hard-working scholar and a university teacher kind to youth. Hence this short recollection of His professional activity.

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Wiesław Skorupski was born on 12 October 1932 in Warsaw. After completion of a secondary school and passing final examinations of the secondary-school certificate he enrolled at the Warsaw University of Technology (WUT). In 1955, being a distinguishing student, he was employed as a junior assistant at the Chair of Chemistry II, Faculty of Chemistry, WUT. After he received, in 1957, his master degree in chemical engineering with specialisation in "chemistry II" (those days this was a code name standing for synthesis of toxic substances, phosphoroorganic pesticides and toxic warfare agents) he was promoted to the rank of an assistant and, subsequently, a senior

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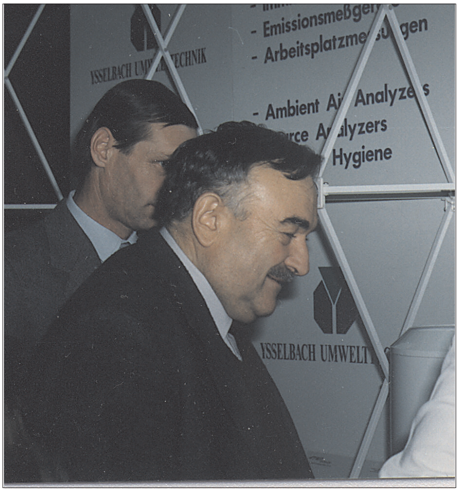
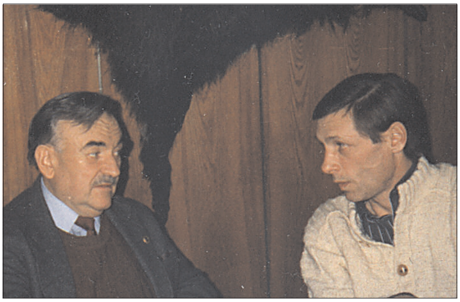
assistant. Within the framework of scientific and research work he developed a number of original syntheses of organic compounds which were to form a basis for his future doctoral thesis written under the guidance of Prof. Stefan Chwaliński, Head of the Chair. Since 1959, working on the waste management, he had cooperated with the Chair of Sanitary Technology, headed by Prof. Zygmunt Rudolf, within the structures of Faculty of Sanitary Engineering (the faculty was reorganized and renamed in 1961 as Faculty of Sanitary and Water Engineering, *ie* FSWE). So, due to liquidation of the Chair of Chemistry II in 1960, he continued his career at FSWE.

As a Master of Science, Wiesław Skorupski got actively involved in teaching, research and laboratory organization work. At that time the Chair of Sanitary Technology conducted some research connected with the ongoing construction of Masovian Refinery and Petrochemical Plants in Plock (renamed in 1999 as the refinery and petrochemical complex run by ORLEN Polish Oil Concern S.A.). His next research efforts focused on viscose waste generated by "*Celwiskoza*" Viscose and Artificial Fibre Works, Jelenia Gora-Cieplice (later known as "*Chemitex-Celwiskoza*" Synthetic Fibre Works, shut down in 1989), which posed a serious technological-ecological problem at that time. In 1965 he defended his doctoral dissertation entitled: *Utilisation of solid waste generated during production of viscose fibre*. Another subject of his research interest during his work at the Chair and later on, after reorganisation of FSWE in 1970, at the Institute of Environmental Engineering was corrosion of construction materials and structures caused by air pollution.

One of the key areas of professional activity for W. Skorupski, Ph.D., Eng. was the protection of the atmosphere. As early as in the middle of the sixties of the previous century, as a chief expert in gaseous air pollutants for the Polish Standardisation Committee, he ran laboratory classes for students in measurement of pollutants emission into the atmosphere. In those days the problem of air pollution attracted attention of and was considered important only by a small group of scientists. It was in this subject area, namely research into chemical contaminants of the atmospheric air, that he gained a broad and lasting recognition among specialists. He contributed to development of emission measurement methods and research into air pollutants imission. He devoted most of his research efforts to this matter.



In the early 80-ties of the previous century the Air Chemistry and Microbiology Team was created within the structures of the Division of Engineering-Sanitary Environmental Protection. The Team was headed by Wieslaw Skorupski Ph.D., Eng. and included also K. Ossowska-Cypryk, Ph.D. and A. Kulig, M.Sc., Eng. In that period of time an intensive research into the environmental impact of municipal management facilities, especially wastewater treatment



plants and waste dumps, was commenced within the framework of, among other things, Governmental Research and Development Programme PR-7 *Management and utilisation of water resources*. Following the creation of the Division of Urban Environment Protection in 1985, the Soil Protection Group (staff: Doctor A. Kulig, J. Pawlowski, M.Sc., W. Rzemek, M.Sc., M. Sternicka-Kantor, M.Sc.) was founded and, originally, the educational and research activity of the latter was managed by W. Skorupski, Ph.D., Eng. However in 1991 he moved on to the Division of Meteorology and Atmosphere Protection of the Institute of Environmental Engineering Systems, where he worked as a senior lecturer for the rest of his life. He published numerous papers on atmosphere protection issues for which he received awards from the then Minister of Administration, Land Management and Environmental Protection, Rector Magnificus of the Warsaw University of Technology and others.

Moreover "mother" Faculty, Doctor W. Skorupski delivered lectures and seminars on environmental protection at many other faculties of the Warsaw University of Technology: *Chemistry*, *Civil Engineering*, *Mechanics and Technology* (at present *Production Engineering*), *Automotive and Construction Machinery Engineering* as well as *Geodesy and Cartography*, including the Institute of Typography. He was invited to lecture at other universities. For many years he delivered lectures and seminars, and promoted M.Sc. theses at the Faculty of Water Protection, Agricultural and Technological Academy of Olsztyn, and at the Faculty of Geology, University of Warsaw. He delivered lectures for participants of numerous postgraduate courses. He was numbered among the most active associates contributing to the organisation of the Staff Training Centre of the Ministry of Environmental Protection, Natural Resources and Forestry in Debe and, subsequently, he was a lecturer at specialised courses for many years there. He delivered lectures (seminars) during training courses on atmosphere protection and other topics in the Training Centre of the Ministry of Chemical Industry. He was numbered among a dozen or so founding members of the Society of Chemistry and Ecological Engineering and then a regular participant of ECOpole conferences for which he prepared papers and at which he always took an active part in official and behind-the-scenes discussions. He was an active member of the Polish Association of Sanitary Engineers and Technicians, he collaborated with the Polish Standardisation Committee, he was a member of the Preventive Sanitary Supervision Commission at the Ministry of Health and Social Care, and acted as an expert for many other organisations, including the judiciary (he described expert's opinions for courts). At the same time Doctor W. Skorupski was a very sincere, kind and hard-working person. He eagerly shared his knowledge, broad experience and unique teaching materials, he obtained from various sources, with others. He was always accessible in the laboratory and managed to find time to provide consultation selflessly, even to outsiders.

His life and professional career were subordinated to teaching university students. He was an excellent teacher and was able to explain, clearly and precisely, many complex issues connected with his specialisation or with general and analytical chemistry: after all, he was, first and foremost, a chemist. In those scarce moments when he was not holding classes with students one could find him in the lab where, until late afternoon or evening hours, he analysed collected research samples or prepared laboratory classes. He was respected by and popular among students of our Faculty, and students of other WUT faculties and other universities, and a vast number of degree candidates, and a lot of environmental protection specialists with whom he kept in touch on professional matters.

Doctor Wiesław Skorupski died on 29 August 1999 and on 6 September His funeral was held at Powązki Cemetery in Warsaw (grave at so-called Old Powązki, sector $315^{\underline{A}}$, row 5). We will remember Him as a kind and modest person who was always there to provide sound advice on difficult matters of work and life.

Andrzej Kulig
Warsaw Technical University

Invitation for ECOpole ’12 Conference

CHEMICAL SUBSTANCES IN ENVIRONMENT

We have the honour to invite you to take part in the 21st annual Central European Conference ECOpole ’12, which will be held in 11–13 X 2012 (Thursday–Saturday) at the Conference Center “Rzemieslnik” in Zakopane, PL.

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

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

The Conference language is English.

Contributions to the Conference will be published as:

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

Additional information one could find on the Conference website:

ecopole.uni.opole.pl

The deadline for sending the Abstracts is **31st August 2012** and for the Extended Abstracts: **1st October 2012**. The actualized list (and the Abstracts) of the Conference contributions accepted for presentation by the Scientific Board, one can find (starting from **31st July 2012**) on the Conference website.

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

At the Reception Desk each participant will obtain abstracts of the Conference contributions as well as the Conference Programme recorded on electronic media (the Programme will be also published on the ECOpole ’12 website).

Further information is available from:
Prof. dr hab. eng. Maria Wacławek
Chairperson of the Organising Committee
of ECOpole ’12 Conference
Opole University
email: Maria.Waclawek@o2.pl
and mrajfur@o2.pl
phone +48 77 455 91 49 and +48 77 401 60 42
fax +48 77 401 60 51

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Prof dr hab. Witold Wacławek,
Editor-in-Chief of Ecological Chemistry and Engineering A
Uniwersytet Opolski
ul. kard. B. Kominka 6
45–032 Opole
Poland
phone +48 77 401 60 42, +48 77 455 91 49
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REDAKTOR TECHNICZNY
Halina Szczegot

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Druk: „Drukarnia Smolarski”, Józef Smolarski, 45–326 Opole, ul. Sandomierska 1. Objętość: ark. wyd. 13,00, ark. druk. 10,50 Nakład: 350 egz. + 5 nadb. aut.