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Monika ARASIMOWICZ[1], Marcin NIEMIEC[1]
and Barbara WIŚNIOWSKA-KIELIAN[1]

ZINC, COPPER AND CHROMIUM CONTENT IN SOILS AND NEEDLES OF THE SCOTS PINE (*Pinus silvestris* L.) FROM THE KRAKOW AGGLOMERATION TERRAIN

ZAWARTOŚĆ CYNKU, MIEDZI I CHROMU W GLEBACH ORAZ SZPILKACH SOSNY ZWYCZAJNEJ (*Pinus silvestris* L.) Z TERENU AGLOMERACJI KRAKOWSKIEJ

Abstract: The aim of the study was to determine soils pollution by heavy metals (Zn, Cu and Cr) and their content in pine needles taken from terrain of Krakow Agglomeration.

It was found large changeability of individual trace metals content in analyzed plants and soils material. The metals content in soils amounted to: 12.64–631.9 mg Zn, 1.24–35.06 mg Cu and 2.39–158.9 mg Cr $\cdot$ kg^{-1} dm. The average content of zinc, copper and chromium in soil samples from the city of Krakow terrain was visibly higher than in the analogous material taken from neighboring localities. Variation coefficients of individual trace elements content were: 102.8 % for Cr, 72 % for Zn and 54.2 % for Cu. The highest amounts of analyzed heavy metals was found in soils from places of Krakow Agglomeration located in zones of large intensity of road traffics and in Old Town where the influence of anthropopressure lasts the longest. High their contents were observed also in soil samples taken from the periphery of Krakow and in localities with dense one-family buildings situated along the main traffic routes. The relatively low content of these metals in soils were observed in multifamily dwelling housing estates and in smaller villages from the periphery of the Agglomeration. On average, the most pollution of studied soils with Cu and Zn was found in the eastern part of the Agglomeration, while the lowest in western one. The highest average Cr content was observed in the soil samples taken from northern part of the Krakow Agglomeration while the lowest in southern part. Contents of zinc and copper in soil were significant positively correlated with organic matter content in soil.

The average contents of analyzed trace metals in pine needles taken from the city of Krakow terrain and from neighboring localities were differed slightly. The average content of these metals in pine needles from the Agglomeration terrain amounted to: 55.45 mg Zn, 4.76 mg Cu and 2.54 mg Cr $\cdot$ kg^{-1} d.m. Individual metals content in plant was differentiated in diverse extent. The largest variation was found in case of Cr (V = 40 %), lower for Zn (V = 30.8 %), and the lowest in case of Cu (26.4 %). The highest average analyzed heavy metals content was found in needles of pine grown in southern part of the Krakow Agglomeration. The smallest Cu and Cr contents were observed in needles taken from the trees grown in northern part of the city and neighboring localities, while the smallest Zn content was noted in samples from the northern part of the Krakow Agglomeration. Obtained results did not prove a substantial correlation between heavy metals content

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in soil and in pine needles, what points at origin of Zn, Cu and Cr from deposition from the atmosphere. The bioaccumulation coefficients of analyzed elements had higher values in case of samples taken from countryside than those taken from city Krakow terrain.

Keywords: heavy metals, soils, pine needles, bioaccumulation

The Krakow Agglomeration constitutes an area of 4069 km^2 composed of 51 communes of the Malopolska province, inhabited by ca 1.45 mln people. Currently, atmospheric air pollution poses one of the main hazards for human beings and the natural environment. Dust and gaseous pollutant emission from industries, classifies this region among the worst in Poland, despite continuous efforts at reducing of pollution. On the other hand, emission originating from the city of Krakow area places the city among the ones most seriously threatened with dust emission. Atmospheric air quality in the Malopolska province is additionally worsened by winds blowing from the west and south-west, which cause pollutants translocation from the Silesia province, which dominates in the pollutant emission in the whole country [1]. Air pollutants including trace metals penetrate to the soil with wet and dry deposition but are also dispersed depending on the direction as well as speed of wind and the temperature [1, 2]. Trace elements which in excessive amounts find their way to the environment pose a serious hazard to plants, animals and man. Therefore, constant monitoring of their contents in individual components of the environment is necessary. Anthropopressure causes major disturbances in element cycle in the nature, leading to pollution of individual components of the environment with them. High contents of heavy metals in soil usually lead to their high concentrations in plants [3], whereas their presence in soil and plants is an indicator of the natural environment quality [4]. Trace elements systematically supplied to the soil accumulate in the topsoil because they are bound by the soil sorption complex and very slowly penetrate into the soil profile [5]. However, plant pollution is usually permanent, what means that elements and chemical compounds accumulated in tissues may remain in them during the whole growth period [4]. Phytoindication is a method based on the use of plants for an assessment of the environment quality and the changes occurring in it. One of the plant species, which is a particularly useful phytoindicator of soil and air pollution, is Scots pine (*Pinus silvestris* L.) [4]. Chemical composition of its needles reflects tree abundance in nutrients but also shows the degree of the environmental pollution. Monitoring conducted using technical methods registers the level and distribution of environmental pollution. Phytoindication supplements the data with the information describing response of living organisms to the level of harmful substances in the environment [6].

The investigations aimed at determining the contents of zinc, copper and chromium in the soil and needles of Scots pine (*Pinus silvestris* L.) collected from the area of the Krakow Agglomeration as a basis for an assessment of anthropopressure level.

Material and methods

Material for the analyses constituted soil samples and pine needles collected from the area of Krakow Agglomeration (Fig. 1).

Fig. 1. Localisation of sampling points

A total 50 samples both of soil and pine needles, including 29 from the Krakow city terrain and 21 from the neighbouring localities within 30 km from the city, were collected in November 2008. The samples were dried at room temperature, whereas the pine needles in a dryer with forced air flow at the temperature of 65 ^{o}C. Total contents of heavy metals in the soil samples were assessed after dry mineralization of organic matter and hot dissolving in a mixture of HNO_3 and $HClO_4$ acids (3:2), whereas in the plant material after mineralization in a mixture of HNO_3 and H_2SO_4 [7]. Metal concentrations in the obtained solutions were determined using ICP-AES method in JY 238 Ultrace apparatus.

Results and discussion

Zinc is an element commonly occurred in the environment. It reveals considerable mobility in the soil from which it is intensively absorbed by plants, what causes that it easily enters both animal and human food chains. In the proper amounts this metal is crucial for proper development of living organisms, whereas in excess it becomes toxic for them. Pollution of the natural environment with zinc is mainly caused by dust pollutant emission from zinc works, coal and waste burning. Zinc also finds its way to soils with phosphorous fertilizers and plant protection preparations [2]. The greatest amount of zinc (631.88 mg $\cdot$ kg^{-1} d.m.) was found in the soil material from Piastowska Street in Krakow and the smallest one (12.64 mg $\cdot$ kg^{-1}) in the samples from Kryspinow (Table 1). The soil samples collected from the most urbanized parts of Krakow (Medweckiego, Stanislawa ze Skalbmierza and Swoszowicka Streets) and from the localities surrounding the city (Wielka Wies, Proszowice, Zabierzow) revealed the largest quantities of this element. The smallest amounts of Zn were noted in the soils of city residential areas (Czarnogorska and Okolna Streets, Oswiecenia estate) and in small villages near Krakow (Raczna, Morawica, Igolomia). Considering the limit contents of heavy metals in the topsoil elaborated by ISSPC [18], 16 % of soil samples revealed the natural Zn content (0^o of pollution), 40 % of soils had elevated Zn content (I^o of pollution), 34 % showed weak (II^o) and 8 % medium pollution (III^o), whereas 2 % of samples revealed strong pollution by this metal (IV^o). Mean content of zinc in the analyzed soil material from the Krakow Agglomeration indicated a weak pollution (II^o) with this element. However, it should be pointed out that average Zn content in the soil samples from the city of Krakow area was much higher than its medium content in the soils collected from the neighbouring localities. Pine needles collected in Krzeszowice town contained the highest Zn amounts – 108.19 mg · kg^{-1} d.m., while the smallest ones were found in the needles of pine growing at Palacha Street in Krakow – 32.1 mg · kg^{-1} dm (Table 1). Zinc content in plants is considered natural within the range from 20 to 100 mg · kg^{-1} d.m. [2]. Following this criterion zinc content in all samples of pine needles may be considered natural.

Copper is a natural trace element of the Earth crust [2]. As a microelement, it is crucial for proper functioning of plants, animals and man. Either a deficiency or excess of copper leads to disturbances of living organism activities and therefore the balance in the environment [9]. In strongly industrialized areas the heaviest contamination of the environment with copper is caused by local mines and metal works processing this metal. Copper concentrations increases in the dust emitted to the atmosphere in city Agglomerations due to intensified road traffic and electric transport [2]. Analogously as in case of zinc, the highest amounts of copper (38 mg · kg^{-1} d.m.) were found in the soil material collected in Piastowska Street in Krakow and the smallest ones (1.24 mg · kg^{-1} d.m.) in the soil from Kryspinow (Table 1).

Table 1

Zn, Cu and Cr contents of soil samples and pine needles and organic matter contents at top soil layer

Sampling points	Pine needles			Soil samples			Organic matter [%]
	Zn	Cu	Cr	Zn	Cu	Cr	
	[mg · kg^{-1} d.m.]						
ul. Pradnicka	44.44	3.68	1.59	176.25	13.00	13.38	2.16
ul. Gornickiego	45.56	2.87	0.82	123.25	12.88	24.06	2.92
ul. S. ze Skalbmierza	50.50	7.94	2.83	402.50	24.25	158.88	4.29
ul. Lepkowskiego	38.00	3.29	2.56	177.50	12.18	39.88	2.47
ul. Powstancow	55.13	5.71	2.10	123.94	14.94	25.63	2.79
os. Oswiecenia	35.44	4.36	2.89	68.13	9.15	13.53	1.97
ul. Makuszynskiego	42.38	5.11	2.19	118.94	11.80	24.38	2.79
ul. Medweckiego	47.09	4.73	2.40	465.63	29.25	30.44	3.77
al. Pokoju	38.06	6.24	2.63	196.88	24.13	33.00	3.33
ul. Cystersow	57.69	5.93	2.97	237.63	25.94	36.94	5.89
ul. Swoszowicka	61.91	5.54	6.35	330.00	9.38	8.05	2.34
ul. Krzywda	67.95	5.18	2.84	133.75	25.13	19.00	4.18

Table 1 contd.

Sampling points	Pine needles			Soil samples			Organic matter [%]
	Zn	Cu	Cr	Zn	Cu	Cr	
	[mg · kg^{-1} d.m.]						
ul. Jerzmanowskiego	33.98	3.90	1.83	211.88	20.31	11.44	3.33
ul. Okolna	36.41	4.22	2.58	44.31	12.23	8.03	1.57
ul. Czarnogorska	58.69	5.26	1.79	43.25	7.05	6.56	1.54
ul. Szwedzka	52.73	6.09	3.66	185.00	23.38	13.05	3.67
ul Wl. Tetmajera	47.51	6.26	1.77	244.38	18.94	20.31	1.92
ul. Jeleniowa	60.15	3.99	3.43	222.50	13.05	22.94	5.65
al. Kasztanowa	35.40	4.25	1.71	148.13	13.69	16.81	3.42
ul. P. Listopadowego	58.65	3.29	2.71	133.13	35.06	15.56	2.57
ul. Juliusza Lea	47.14	4.72	1.81	141.88	28.81	11.93	6.46
ul. Lindego	46.81	5.01	3.98	157.50	24.13	11.66	5.13
ul. Na Blonie	54.25	5.39	4.65	93.31	7.21	10.16	4.55
ul. Majora Lupaszki	48.00	3.83	1.80	186.88	16.88	16.69	3.99
ul. Palacha	32.10	4.08	1.26	130.63	16.69	10.96	2.92
ul. Piastowska	40.50	4.30	2.13	631.88	38.00	12.13	4.58
ul. Nad Sudolem	46.06	5.09	3.47	147.50	10.79	10.37	2.39
ul. Pachonskiego	68.19	3.26	1.17	95.25	10.25	22.31	2.90
ul. Pasteura	51.13	4.09	1.48	80.00	8.50	9.58	2.15
Zielonki	95.56	4.63	2.34	97.81	9.59	12.53	5.25
Maslomiąca	71.94	4.62	3.19	77.63	5.69	22.44	3.04
Iwanowice	63.56	3.99	2.16	105.69	12.22	18.19	2.72
Slomniki	36.75	2.34	2.14	101.75	13.31	26.69	3.86
Kocmyrzow	50.38	4.41	2.01	175.63	15.69	26.38	8.28
Koniusza	61.88	5.42	2.19	209.38	11.04	29.38	3.52
Proszowice	63.31	4.73	3.42	253.00	28.94	31.88	2.97
Karwin	37.00	4.68	3.60	77.13	12.71	13.69	4.05
Igolomia	29.56	2.56	3.57	59.44	11.89	15.25	2.14
Niepolomice	59.88	4.90	1.98	203.75	17.00	31.81	4.21
Wieliczka	95.56	6.05	2.96	147.50	19.50	20.31	7.50
Mogilany	69.50	4.96	1.61	72.63	10.62	18.44	4.56
Skawina	76.06	9.63	3.46	162.50	31.25	14.38	2.57
Raczna	60.38	5.17	3.37	25.13	3.39	4.16	1.26
Kryspinow	64.56	5.72	3.86	12.64	1.24	2.39	0.56
Liszki	57.94	3.41	2.72	70.50	9.44	16.56	1.75
Morawica	47.69	4.18	1.58	34.88	5.18	16.75	1.49
Zabierzow	73.38	5.67	3.03	233.75	14.81	11.36	4.10
Krzeszowice	108.19	4.99	1.28	51.69	5.20	8.25	1.33
Skala	87.50	4.03	1.75	155.63	6.44	26.44	2.22
Wielka Wies	60.19	4.44	1.30	350.63	23.00	33.44	3.47
Average	**55.45**	**4.76**	**2.54**	**162.61**	**15.70**	**21.17**	**3.37**
CV [%]	**30.80**	**26.50**	**40.00**	**72.00**	**54.20**	**102.80**	**46.90**

Relatively large quantities of copper were registered in the soils from the city area (Powstania Listopadowego, Medweckiego and Lea Streets) but also in town around Krakow (Skawina and Proszowice). The localities mentioned above are characterized by compact settlement pattern and busy traffic routes running in their vicinity. Copper content in the analyzed soils of Krakow Agglomeration pointed to only slightly elevated content of this element (I^o of pollution) on a six degree scale proposed by ISSPC [8], of which 72 % of soils revealed natural content (0^o) and 28 % had elevated Cu concentrations (I^o). Average copper content in the Agglomeration soils was 15.7 mg · kg^{-1} d.m. (Table 1) and was approximate (the same level of pollution) to average Cu contents registered in the research conducted by Gambus [10] on the soils of the former Krakowskie province. Copper content in aboveground parts of the plant is quite diversified and depends on many factors (species, kind of soil, antagonism with other elements), therefore it is difficult to determine the limit numbers for its natural content in tissues and toxicity threshold. As reported by Kabata-Pendias and Pendias [2], an average Cu content in aerial part o the plants fluctuates from 5 to 20 mg · kg^{-1} d.m. Mean copper content in pine needles growing in the Krakow Agglomeration area was 4.76 mg · kg^{-1} d.m. The greatest amounts were found in pine needles growing in places with highly intensive traffic, close to busy traffic routes (Skawina and Tetmajera Street in Krakow, Pokoju Avenue in Krakow), while the smallest were noted in small villages outside the city boundaries (Slomniki, Igolomia).

Chromium is a natural component of the Earth's crust. This element is present in various quantities and its natural content in soil fluctuates from trace amounts to over 0.1 %. Its role in plant growth and development has not been fully identified. However, chromium is indispensable for life to animals and humans but excessive its concentrations are harmful to all living organisms. Despite many anthropogenic sources of chromium pollution, there is no risk of global contamination of the natural environment with this metal. However, this element may be introduced into the environment components locally, which may cause its excessive entering the biogeochemical cycle [2, 9]. Similarly as for Zn and Cu the smallest quantities of Cr were found in the soil samples collected in Kryspinow (2.39 mg · kg^{-1} d.m.), whereas about 70 times bigger were assessed in Stanislawa ze Skalbmierza Street in Krakow (158.88 mg · kg^{-1} d.m.) (Table 1). Considerable amounts of this element were also found in soil samples collected in Lepkowskiego and Cystersow Streets, in Pokoju Avenue and in Medweckiego Street in Krakow, but also in Wielka Wies, Proszowice and Niepolomice localities. It was also found that 84 % of the collected samples revealed natural content of chromium (0^o of pollution), 14 % had increased content of this metal (I^o) and 2 % revealed medium pollution with this metal (III^o). Mean chromium content noted in the Agglomeration soils was 21.17 mg · kg^{-1} d.m., which according to the West European criteria classifies these soils to clean ones [9]. The least of chromium (0.82 mg · kg^{-1} d.m.) was assessed in needle samples of pine growing in Gornickiego Street in Krakow whereas the greatest amounts were found in Swoszowicka Street (6.35 mg · kg^{-1} d.m.) (Table 1). Average content of chromium in pine needles growing in the Krakow Agglomeration area, ie 2.54 mg · kg^{-1} d.m. is higher than average content of this element in plants for consumption (0.02–1 mg · kg^{-1} d.m.) stated by Kabata-Pendias and Pendias [2].

The contents of the analyzed heavy metals (Zn, Cu and Cr) in the soil material collected from the area of the Krakow Agglomeration were diversified to various degrees. The highest variability was assessed for Cr (coefficient of variation, CV = = 102.8 %), slightly smaller for Zn (CV = 71.2 %) and the lowest for Cu (54.2 %). Similar diversification of the studied trace element values may be observed in soils of other agglomerations in Poland [11]. Also in the collected pine needles chromium content revealed the greatest variability (V = 40 %), then zinc (V = 30.8 %), while the lowest value of variability coefficient was registered for copper (V = 26.4 %). The reason for such considerable variability of the analyzed elements content might be the locally uneven distribution of soil and atmospheric air pollution with heavy metals. Heavier pollution with zinc, copper and chromium is usually observed along traffic routes and within a radius of several hundred meters from factories. The changeability is also caused by climatic factors such as wind or temperature [1].

According to the literature of the subject, there are numerous factors affecting phytoavailability and trace metal contents in the arable layer. The most frequently mentioned soil physicochemical properties which influence the metal availability include: type and granulometric composition of soil, organic matter content, sorption capacities as well as pH and oxidation-reduction potential [12]. According to Siuta [9] there is a positive correlation between organic matter content in soil and the amount of trace elements retained in its top layer. Obtained results confirmed the thesis, as evidenced by the values of correlation coefficients between organic matter content and the quantity of heavy metals determined in soil. The contents of Zn and Cu were positively correlated with organic matter content in soils. The correlation coefficients were respectively $r_{0.05} = 0.32$ and $r_{0.01} = 0.42$. Similar dependence was not found for Cr in the studied soils of Krakow Agglomeration. No significant correlation was found either between heavy metal content in the soil and needles of pines growing in the individual places. It points out on origin of Zn, Cu and Cr from the atmospheric deposition. According to Siuta [9], there are numerous factors conditioning heavy metal absorption by plants. Gorlach [13] also states that various species and even varieties of plants growing under the same conditions may reveal different ability of heavy metal uptake from soil. Other authors state, that the soil content of heavy metal forms available to plants is also affected by the course of climatic conditions, which to a considerable degree modify the soil properties and therefore influence the level of these elements content in plants [14]. Moreover, Siuta [9] emphasizes that in practice heavy metal concentrations are assessed only in the topsoil. For this reason, most frequently no dependence is assessed between the elements content in soil and their concentrations in plants, especially perennials.

Intensity and scale of soil and plant pollution with trace elements depends on many local factors, however a serious source of heavy metals deposited on the soil and plant surface is so called far emission connected with pollutants dispersion and translocation for long distances [15]. Climatic conditions (precipitation, temperature, wind direction and strength) also play an important role in pollutant dispersion. Analysis of soil samples pollution revealed the highest medium pollution with Zn and Cu in the eastern part of Krakow Agglomeration, whereas Cr contamination was the highest in the northern part. Average lowest contents of all analyzed elements were registered in the southern part of the Krakow city and in the eastern part of the neighboring localities. It may be due to the fact that winds from the west and south west prevail in the area of Krakow and its neighborhood, which causes a dispersion of pollutants from the west and south towards the east and north. On the other hand, the highest average speeds are noted for the winds from the west [1]. Analysis of the chemical composition of pine needs showed the highest mean contents of all studied elements in the material collected in the southern part of Krakow Agglomeration. Pine needles taken in the eastern part of the Agglomeration contained the lowest quantities of zinc, whereas the least amounts of copper and chromium were determined in pine needles growing in the northern part of this region.

Bioaccumulation coefficient (BC) expresses the ratio of element concentration in plant to its content in soil. Analysis of the obtained BC values for Zn, Cu and Cr demonstrated that under conditions of soil pollution with heavy metals needles more easily cumulate Zn and Cu, than Cr. Zinc is an element very easily absorbed by plants from the soil, therefore Zn bioaccumulation coefficient assumed the highest values among the studied elements both in the city of Krakow and in the other research points situated in the neighboring areas. It is caused by a relatively considerable mobility of this element in the soil, including its exchangeable forms and compounds with organic matter. It has been confirmed by the highest mean value of bioaccumulation coefficient for zinc 0.71 in comparison with BC 0.5 for Cu and 0.21 for Cr. On the other hand the lowest BC value noted for chromium is caused by a poor translocation of this element from soil to plant tissues [9]. On average, bioaccumulation coefficient for Zn, Cu and Cr assumed higher values for rural areas as compared with the city (Fig. 2).

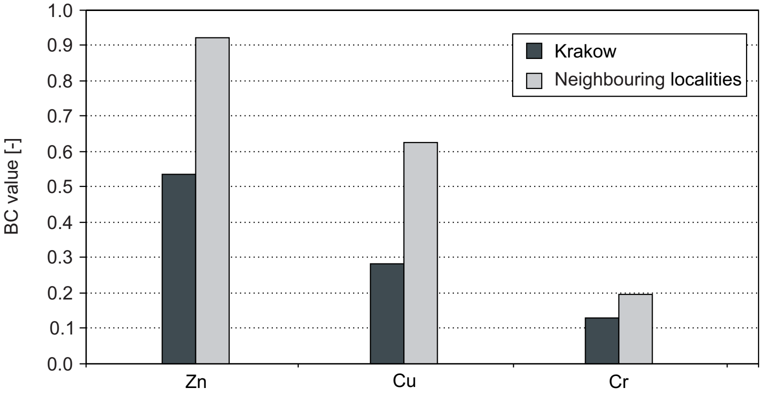

Fig. 2. Average values of bioaccumulation coefficient of metals in pine needles

Conclusions

1. The Zn, Cu and Cr content in soils and pine needles taken from Krakow Agglomeration showed large changeability. Significantly higher amounts of individual elements were observed in places of large intensity of road traffics and in Old Town, as well as in the larger localities nearby Krakow.

2. The average Zn, Cu and Cr content in soil samples taken from Krakow was visibly higher than in the material taken from neighboring localities.
3. The average contents of Zn, Cu and Cr in pine needles taken from Krakow terrain and from neighboring localities were differed slightly and pointed at their natural content.
4. The highest average contents of analyzed metals were found in needles of pine grown in southern part of Krakow Agglomeration.
5. On average, the biggest pollution of soils with Cu and Zn was found in the eastern part of the Agglomeration, while Cr in northern one.
6. Contents of Zn and Cu in soil were significant positively correlated with organic matter content in soil.
7. The bioaccumulation coefficients had higher values in case of samples taken from neighboring localities than those taken from city Krakow terrain.
8. Obtained results did not prove a substantial correlation between heavy metals content in soil and in pine needles, what may point at absorption of metals deposed from the atmosphere.
9. Needles of the Scot pine are good indicator of environment pollution level.

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ZAWARTOŚĆ CYNKU, MIEDZI I CHROMU W GLEBACH ORAZ SZPILKACH SOSNY ZWYCZAJNEJ (*Pinus silvestris* L.) Z TERENU AGLOMERACJI KRAKOWSKIEJ

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Abstrakt: Celem pracy było określenie zanieczyszczenia gleb metalami ciężkimi (Zn, Cu i Cr) oraz ich zawartości w szpilkach sosen z terenu aglomeracji krakowskiej.

Stwierdzono duże zróżnicowanie zawartości poszczególnych metali śladowych w analizowanym materiale glebowym i roślinnym. Gleby zawierały: 12,64–631,88 mg Zn, 1,24–38 mg Cu oraz 2,39–158,9 mg Cr · kg^{-1} s.m. Średnie zawartości cynku, miedzi i chromu w próbkach glebowych z terenu miasta Krakowa były wyższe niż w analogicznym materiale pobranym z okolicznych miejscowości. Współczynniki zmienności zawartości poszczególnych metali przyjmowały wartości: 102,8 % dla Cr, 72 % dla Zn i 54,2 % dla Cu. Najwięcej metali zawierały gleby pobrane z punktów aglomeracji krakowskiej, zlokalizowanych w rejonach o dużym natężeniu ruchu drogowego oraz na terenie Starego Miasta, które najdłużej podlegają antropopresji. Duże ich zawartości zanotowano także w próbkach gleb pobranych na obrzeżach Krakowa oraz w miejscowościach o zwartej zabudowie domów jednorodzinnych, usytuowanych przy głównych szlakach komunikacyjnych. Stosunkowo mało tych metali zawierały gleby z osiedli o zabudowie wielorodzinnej oraz z mniejszych wsi położonych na obrzeżach aglomeracji. Średnio największe zanieczyszczenie badanych gleb Zn i Cu stwierdzono we wschodniej części aglomeracji, a najmniejsze w części zachodniej. Największą średnią zawartością Cr odznaczały się gleby z północnej, a najmniejszą z południowej części aglomeracji krakowskiej. Zawartość cynku i miedzi w glebie były istotnie dodatnio skorelowane z zawartością materii organicznej.

Średnie zawartości badanych metali śladowych w szpilkach sosen pobranych z terenu miasta Krakowa oraz z pobliskich miejscowości różniły się nieznacznie. Przeciętna zawartość tych metali w igliwiu sosen rosnących na terenie aglomeracji wyniosła: 55,45 mg Zn, 4,76 mg Cu i 2,54 mg Cr · kg^{-1} s.m. Zawartości poszczególnych metali ciężkich były zróżnicowane w niejednakowym stopniu. Największą zmienność stwierdzono w przypadku Cr (V = 40 %), następnie Zn (V = 30,8 %), a najmniejszą w przypadku Cu (26,4 %). Średnio najwięcej wszystkich analizowanych metali stwierdzono w szpilkach sosen rosnących w południowej części aglomeracji krakowskiej. Najmniej Cu i Cr zawierały igły pobrane z drzew z północnej części miasta oraz z graniczących z nią miejscowości, natomiast najmniejszą zawartość Zn zanotowano w próbkach pobranych w północnej części aglomeracji. Nie wykazano statystycznie istotnej korelacji między zawartością badanych metali w glebie i igliwiu sosny, co wskazuje na ich pobieranie z depozycji z atmosfery. Współczynniki bioakumulacji badanych metali przyjmowały znacznie większe wartości w przypadku próbek pobranych na terenach wiejskich w porównaniu z pobranymi na terenie miasta Krakowa.

Słowa kluczowe: metale ciężkie, gleby, szpilki sosny, bioakumulacja

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EFFECT OF BOTTOM DEPOSIT SUPPLEMENT ON TRACE ELEMENT CONTENT IN LIGHT SOIL

WPŁYW DODATKU OSADU DENNEGO NA ZAWARTOŚĆ PIERWIASTKÓW ŚLADOWYCH W GLEBIE LEKKIEJ

Abstract: The research aimed at an assessment of bottom deposit supplement effect on the content and mobility of selected trace elements in light soil. The investigations demonstrated a positive effect of bottom deposit on increasing light soil pH. After a two-year research period the soil pH was 6.24 on the control treatment, 6.49 on the treatment with a 5 % supplement of the deposit and 6.86 on the treatment containing 10 % of the deposit. Bottom deposit supplement to light soil significantly diminished the content of zinc, lead and manganese available forms extracted with 1 mol HCl · dm^{-3} and bioavailable forms of cadmium, manganese and iron extracted with 0.01 mol $CaCl_2$ · dm^{-3}. No apparent influence of the soil pH on diminishing the availability of a majority of analyzed elements was found, which has been confirmed by negative and insignificant values of correlation coefficients between pH value and element content in soil.

Keywords: bottom deposit, trace elements, light soil, 0.01 mol $CaCl_2$ · dm^{-3} extract, 1 mol HCl · dm^{-3} extract

Dredging water reservoirs is a commonly used measure allowing to maintain them in a proper state so that they fulfill their economic and environmental functions [1–3]. In pursuance of the regulation of the Minister of the Natural Environment [4], bottom deposit (the output) is a waste marked with 1705 code, which requires an appropriate management. The research conducted by Wisniowska-Kielian and Niemiec [5] revealed that the extracted deposits, showing a neutral or alkaline reaction and high fraction of silt and clay fractions, may be used for an improvement of physicochemical properties of light and acid soils. On the other hand, Pelczar et al [6] report that despite high content of fertilizer substances, bottom deposits are unsuitable for agricultural application because of heavy metal contamination. These deposits should be used as a material

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for reclamation of mine waste landfills and fly ash disposal sites [6]. At this point it should be mentioned that the form in which trace elements occur in soils (total or soluble) or in bottom deposits are very important from ecological viewpoint because some are toxic (Pb, Cd) and in excess all are harmful for living organisms. Frequently total element contents are considered and used for indications of the degree of soil environment contamination [7]. However, total contents are not the best indicator of element availability and mobility in soil. Therefore an analysis of bioavailable element form concentrations seems justified, since they are a potential source of minerals for plants and may pose a hazard for the soil environment when they are too high. The research aimed at an assessment of the effect of bottom deposit on the content and mobility of selected trace elements in light soil.

Material and methods

A two-year pot experiment (2006–2007) was conducted on light soil with granulometric composition of weakly loamy sand (Tables 1, 2). The bottom deposit originated from a small retention reservoir located in Zeslawice village at 8.7 km of the Dlubnia River course (Malopolska province) [8].

Table 1

Characteristics of selected properties of soil and bottom deposit

Component	pH_{KCl}	C org.	N total	P_2O_5	K_2O
		[$g \cdot kg^{-1}$ d.m.]		[$mg \cdot kg^{-1}$ d.m.]	
Soil	6.21	9.37	0.36	78.70	165.96
Bottom sediment	7.35	15.80	1.0	44.61	69.76

Table 2

Contents of heavy metals in soil and bottom deposit

Component	Cr	Zn	Pb	Cu	Cd	Ni	Fe	Mn
	[$mg \cdot kg^{-1}$ d.m.]							
Soil	5.93	62.0	29.75	4.00	0.68	4.15	3010	150
Bottom sediment	15.0	76.31	12.85	12.23	0.35	11.0	7550	140

The material was qualified to ordinary silt deposit group with $pH_{KCl} = 7.35$. Moreover the deposit revealed low content of bioavailable phosphorus and potassium but high content of magnesium. According to standards concerning the quality of bottom deposits, heavy metal concentrations in the analyzed deposit did not exceed the content permissible for the output [9] or for group B soil and earth [10]. According to the IUNG assessment, comprising a 6-degree soil classification regarding heavy metal concentrations, considering the reaction and granulometric composition, the analyzed deposit, revealed the natural contents (degree 0). On the other hand, according to the limit heavy metal contents, the soil used for the experiment showed elevated content of Zn and Cd (degree I) [7]. The experimental design comprised 3 treatments in 4 replications: soil without bottom deposit (control) (I), soil with a 5 % supplement of bottom deposit (II) and soil with a 10 % addition of the deposit (III). Equal NPK fertilization was applied on all treatments in doses respectively: 1.8 g N; 1.1 g P; 2.2 g K per pot (8 kg of soil d.m.). Mineral salts as NH_4NO_3; KH_2PO_4 and KCl were applied once before the test plant (maize) sowing. Air-dried bottom deposit was added to the soil in the first year of the investigations.

In the soil samples collected in the second year of the experiment pH was assessed in 1 mol KCl $\cdot$ dm^{-3} by potentiometer and the content of selected trace elements (iron, manganese, zinc, copper, nickel, chromium, lead and cadmium) was determined. Total element content in soil was assessed after hot mineralization in the mixture of HNO_3 and $HClO_4$ acids (2:1). The soluble forms of Zn, Cu, Ni, Pb, Cr, Cd, Fe and Mn were extracted from the soil with 1 mol $\cdot$ dm^{-3} HCl solution (Rinkis method) and with 0.01mol $\cdot$ dm^{-3} $CaCl_2$ solution [11–13]. Extraction of the soluble element forms was conducted at the soil to solution ratio 1:10 and during extraction lasting 1 hour (1 mol HCl $\cdot$ dm^{-3}) and 2 hours (0.01 mol $CaCl_2$ $\cdot$ dm^{-3}). The element concentrations in the solutions were assessed using ICP-AES apparatus (JY 238 ULTRACE, Jobin Yvon). The obtained results were verified statistically using one-way ANOVA at significance level $\alpha = 0.05$, by means of Statistica 8.1 programme.

Results and discussion

In conditions of acid soil reaction solubility of most elements toxic for plants increases, whereas solubility of main nutrients decreases [14, 15]. After a two-year period of investigations the soil pH, depending on the experimental treatment, was 6.42 on the control, 6.49 on the treatment with a 5 % bottom sediment supplement and 6.86 on the treatment with a 10 % sediment addition. Therefore, bottom deposit supplement to the soil caused an increase in light soil pH value by 17 % (5 % deposit supplement) and by 23 % (10 % addition of the sediment) in relation to the control treatment, whereas the increase reached 5 and 10 % in comparison with the initial soil.

The effect of bottom sediment admixture on the content and mobility of the analyzed trace elements was shown in Table 3. Total content of zinc in the soil after the experiment completion was not significantly diversified and fluctuated from 61.54 to 62.34 mg $\cdot$ kg^{-1} d.m. On the other hand, bottom deposit supplement to the soil markedly diversified the content of this metal forms soluble both in 0.01 mol $CaCl_2$ and in 1 mol HCl $\cdot$ dm^{-3} (Table 3). On the treatments with 5 % and 10 % share of the bottom deposit, on average 44 % and 45 % increase in zinc forms soluble in 0.01 mol $CaCl_2$ $\cdot$ dm^{-3} extract was assessed in comparison with the control. On the other hand under the influence of 1 mol HCl $\cdot$ dm^{-3} a decreased availability of this metal was observed by 41 % (at 5 % of the deposit addition) and by 26 % (at 10 % of bottom deposit). The share of soluble zinc forms extracted with 0.01 mol $CaCl_2$ $\cdot$ dm^{-3} was between 23 and 33 % and extracted with 1 mol HCl $\cdot$ dm^{-3} between 44 % and 75 % of this element total content (Fig. 1).

Table 3

Contents of heavy metals in soil after 2nd year of the experiment [mg · kg^{-1} d.m.]

Treatment	Zn	Cu	Ni	Cr	Cd	Pb	Fe	Mn
0.01 mol $CaCl_2 \cdot dm^{-3}$								
Soil without sediment	14.20	1.57	0.40	0.20	0.56	13.78	221.25	64.13
Soil+ 5 % sediment	20.50	1.37	0.24	0.19	0.46	10.38	124.75	40.03
Soil + 10 % sediment	20.53	1.83	0.57	0.22	0.48	10.82	145.50	46.13
$LSD_{0.05}$	1.77	ns*	ns	ns	0.05	1.13	31.13	10.84
1 mol $HCl \cdot dm^{-3}$								
Soil without sediment	46.50	2.34	0.48	0.65	0.64	21.37	836.19	100.58
Soil + 5 % sediment	27.65	2.35	0.34	0.64	0.49	18.79	784.29	84.49
Soil + 10 % sediment	34.55	2.26	0.59	0.80	0.50	19.76	891.87	98.70
$LSD_{0.05}$	10.14	ns	ns	0.07	ns	1.45	ns	9.89
Total content								
Soil without sediment	61.54	4.48	4.13	5.88	0.76	26.03	3432.2	137.64
Soil+ 5 % sediment	62.34	5.40	4.55	6.81	0.51	22.25	3530.9	137.60
Soil + 10 % sediment	61.91	4.90	4.10	6.58	0.56	22.36	3718.4	141.50
$LSD_{0.05}$	ns	0.67	0.24	ns	0.09	ns	ns	ns

ns – statistically nonsignificant.

Both doses of bottom sediment added to the soil significantly increased the total copper content. On the treatments which received 10 % share of the deposit the increase was 9 % and on the treatments with 5 % deposit share – 21 % in comparison with the soil without the deposit (Table 3). The soil concentrations of soluble copper forms were not markedly diversified depending on the percent share of the bottom deposit in the soil. Copper soluble in 0.01 mol $CaCl_2 \cdot dm^{-3}$ constituted between 25 and 37 % of this metal total content. However, in effect of 1 mol $HCl \cdot dm^{-3}$ copper solubility generally diminished in the direction of: control treatment > 10 % deposit supplement > 5 % deposit supplement and constituted from 44 % to 52 % of the total copper content in the researched soil (Fig. 1).

Total content of nickel in soil after the finished experiment was significantly diversified depending on bottom sediment addition to the soil and fluctuated from 4.10 mg to 4.55 mg · kg^{-1} d.m. The highest content of this metal was assessed on the treatment with a 5 % deposit supplement, whereas the lowest on the treatment with its 10 % share. Bottom deposit did not significantly diversify nickel soluble forms content in the soil (Table 3). The share of nickel forms soluble in 0.01 mol $CaCl_2 \cdot dm^{-3}$ ranged from 5 to 14 % of its total content. Available forms of nickel determined in 1 mol $HCl \cdot dm^{-3}$ were on a similar level and ranged from 7 to 14 % of this metal total content (Fig. 1).

The investigations did not demonstrate any marked effect of bottom deposit on total content of chromium and its soluble forms determined in 0.01 mol $CaCl_2 \cdot dm^{-3}$ extract

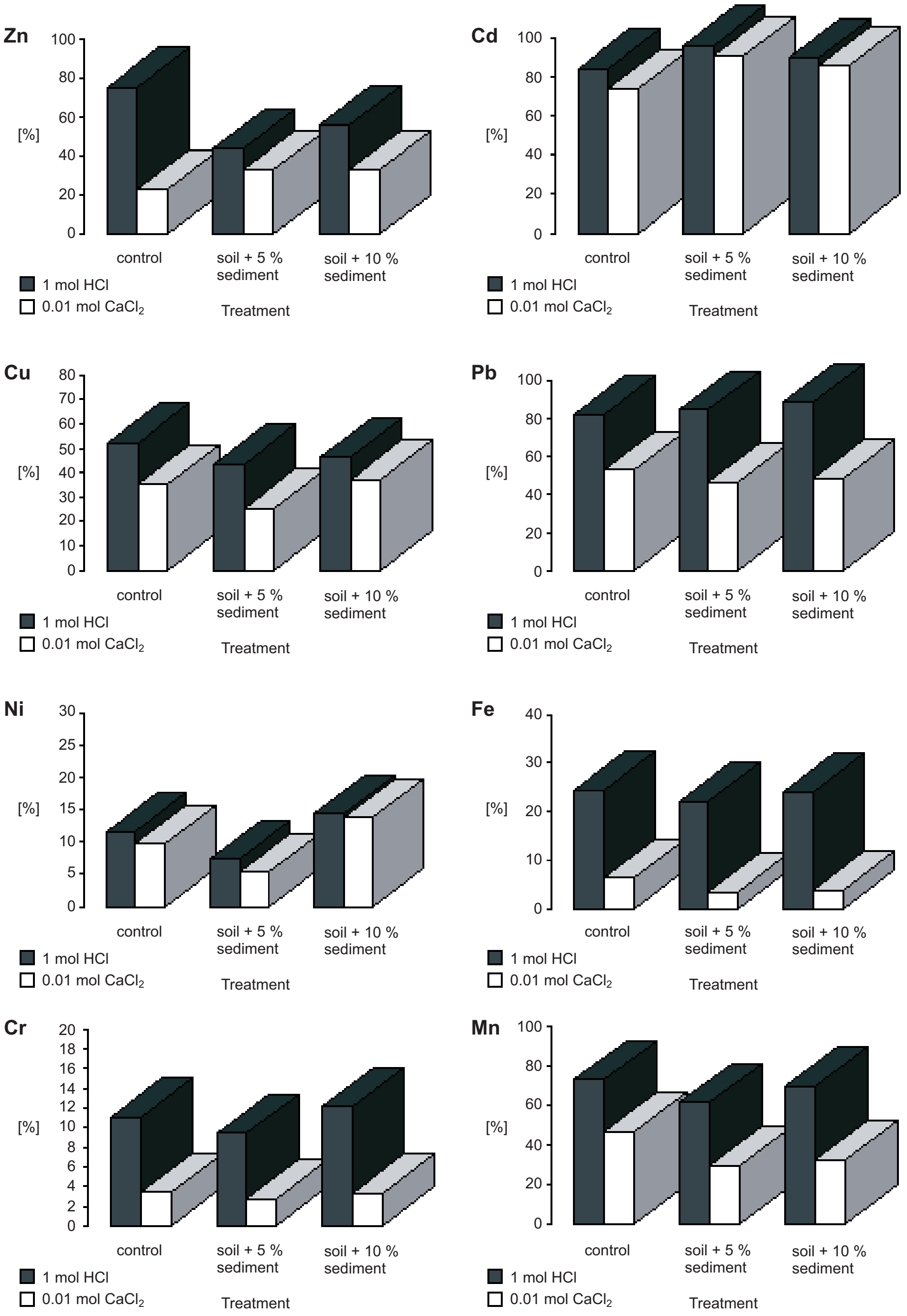

Fig. 1. Percent share of available forms of trace elements in their total contents in soil

(Table 3). The highest value of available chromium forms was found on the treatment with a 10 % addition of bottom sediment, however for extraction with 1 mol HCl $\cdot$ dm^{-3} the dependence was statistically significant. The content of soluble chromium forms in soil constituted from 2.8 to 3.4 % (0.01 mol $CaCl_2$ $\cdot$ dm^{-3}) and from 9 to 12 % (1 mol HCl $\cdot$ dm^{-3}) of this element total content in the researched soil (Fig. 1).

An apparent decline in total cadmium content in relation to the control treatment was demonstrated in the soil with a 5 % share of the deposit, where it diminished by 33 % and in the soil with 10 % deposit supplement showing a 26 % decrease. An admixture of bottom sediment to the soil also affected diminishing the content of this element soluble forms and the dependencies were significant for the extraction with 0.01 mol $CaCl_2$ $\cdot$ dm^{-3} (Table 3). On the treatments with a 5 % deposit admixture a 18 % decrease in cadmium soluble forms in soil was revealed (0.01 mol $CaCl_2$) and a 23 % decline (for 1 mol HCl extraction), whereas on the treatments with a 10 % deposit share, respectively 14 % and 22 % decrease. Generally the soluble cadmium forms content in soil was diminishing in the direction of: control treatment > 10 % deposit supplement > 5 % deposit supplement. Soluble forms of cadmium determined in 0.01 mol $CaCl_2$ $\cdot$ dm^{-3} constituted between 74 and 90 % of this metal total content in soil, whereas determined in 1 mol HCl $\cdot$ dm^{-3} made up between 84 and 96 % (Fig. 1).

When the experiment was completed, total lead content in soil was not significantly diversified in result of bottom sediment admixture and fluctuated from 22.25 to 26.03 mg $\cdot$ kg^{-1} d.m. Application of bottom sediment to the soil significantly diversified the content of this metal soluble forms (Table 3). The treatments with 5 % and 10 % share of bottom deposit revealed a decrease in lead soluble forms content in soil respectively by 25 % and 21 % (0.01 mol $CaCl_2$ $\cdot$ dm^{-3}) and by 12 % and 24 % (1 mol HCl $\cdot$ dm^{-3}) in relation to the treatment without the deposit. Lead forms extracted with 0.01 mol $CaCl_2$ $\cdot$ dm^{-3} constituted between 47 % and 53 %, and those extracted with 1 mol HCl $\cdot$ dm^{-3} from 82 % to 84 % of this metal total concentration (Fig. 1).

Both doses of applied bottom deposit slightly increased total content of iron in soil (Table 3). Also the content of iron soluble forms assessed in 1 mol HCl $\cdot$ dm^{-3} was not dependent significantly on bottom sediment admixture and was diminishing in the direction of: a 10 % deposit addition > control treatment > a 5 % sediment addition. On the other hand, application of bottom deposit to the soil apparently increased the content of this metal bioavailable forms determined in 0.01 mol $CaCl_2$ $\cdot$ dm^{-3} (Table 3). On the treatments with a 5 % supplement of bottom deposit to the soil iron content decreased by 44 % and on treatments with a 10 % admixture by 34 % in comparison with the control. Iron forms soluble in 0.01 mol $CaCl_2$ constituted between 4 % and 6 % of this metal total content in soil, whereas those soluble in 1 mol HCl $\cdot$ dm^{-3} between 22 % and 24 % (Fig. 1).

Total content of manganese in soil after the experiment has been competed fluctuated from 137.64 to 141.50 mg $\cdot$ kg^{-2} d.m. An admixture of bottom deposit to the soil significantly decreased the content of this metal forms soluble both in 0.01 mol $CaCl_2$ and in 1 mol HCl $\cdot$ dm^{-3} in comparison with the control (Table 3).On the treatment where 5 % and 10 % of bottom sediment was applied a decline respectively by 38 and 28 % in solubility of manganese determined in 0.01 mol $CaCl_2$ $\cdot$ dm^{-3} was found. On the other hand, in effect of 1 mol HCl $\cdot$ dm^{-3} a 15 % decrease in this metal bioavailability was registered (for a 5 % deposit addition) and by 2 % (for a 10 % deposit admixture) in comparison with the control. The share of soluble forms of manganese extracted with 0.01 mol $CaCl_2$ $\cdot$ dm^{-3} was from 29 % to 47 %, whereas the forms extracted with 1 mol HCl $\cdot$ dm^{-3} made up between 61 and 73 % of this element total soil concentrations (Fig. 1).

The process of learning mineral biovailability is important in view of proper plant supply with these components. The issue of trace element bioavailability, which should be addressed is an assessment of their readily soluble forms. It is obvious that element content in plants is the bigger, the more numerous easily available forms of these elements are present in soil [12, 16]. The presented investigations applied a non-specific method using two extraction solutions: 1 mol HCl and $CaCl_2$ $\cdot$ dm^{-3} for the extraction of trace element available forms from the soil mixed with bottom deposit. Application of the test with 1 mol HCl $\cdot$ dm^{-3} is a routine procedure, commonly used by chemical--agricultural stations and by IUNG for the assessment of trace element available forms content in soils [17]. Also the 0.01 mol $CaCl_2$ $\cdot$ dm^{-3} test suggested by Houba et al [13] as a physiological soil solution balanced with the soil solution which may be used for an assessment of nutrient availability to plants [12, 18]. Moreover, according to many authors the 0.01 mol $CaCl_2$ $\cdot$ dm^{-3}, unlike 1 mol $\cdot$ dm^{-3} is counted among solutions with low extraction powers and determining so called bioavailable (active) fraction of trace elements [19,16]. According to expectations in the presented investigations smaller amounts of the analyzed elements were found in the 0.01 mol $CaCl_2$ $\cdot$ dm^{-3}. The content of zinc in this extract was between 26 % and 69 % lower, copper between 19 % and 24 %, nickel from 3 % to 29 %, chromium from 69 % to73 %, cadmium 4–16 %, lead 36–45 %, iron from 74 % to 84 % and manganese from 36 % to 53 % in relation to the studied element content in 1 mol HCl $\cdot$ dm^{-3} extract. Generally, hydrochloric acid leaches metals bound to exchangeable, carbonate, Fe/Mn oxides and organic matter fractions. Moreover, as reported by Dziadek and Waclawek [15], in case of strongly polluted soils, extraction with such strong substance as 1 mol HCl $\cdot$ dm^{-3} does not show the real hazard for plants. It has been commonly accepted that copper, lead, chromium and nickel are the least mobile elements in soil, while zinc and cadmium are counted among the most mobile, whereas manganese and iron place in between them [14]. Mobility of the elements analyzed in the presented investigations looked as follows: Cd > Pb > Mn > Zn > Cu > Fe > Ni = Cr (1 mol HCl $\cdot$ dm^{-3}) and Cd > Pb > Zn > Mn = Cu > Ni > Cr > Fe (0.01 mol $CaCl_2$ $\cdot$ dm^{-3}). It was also demonstrated that bottom deposit supplement to light soil diminished the content of available forms of zinc, cadmium, lead, iron and manganese extracted with 1 mol HCl $\cdot$ dm^{-3} and copper, nickel and chromium (a 5 % admixture of bottom deposit), cadmium, lead, iron and manganese extracted with 0.01 mol $CaCl_2$ $\cdot$ dm^{-3} in relation to these elements content in the soil without the deposit supplement. Numerous investigations have shown that soil reaction, humus content and granulometric composition may affect trace element mobility and therefore their uptake by plants. Increased mobility, particularly of heavy metals in the environment influences their greater accumulation in plants posing a grave hazard for living organisms. According to a prevailing opinion, trace elements may pass into less soluble forms at higher pH values, which leads to their uptake by plants and diminishes their toxicity for plants [20]. Presented research did not find any significant effect of soil pH on diminishing the availability of most analyzed elements. The fact was confirmed by the negative, but insignificant values of correlation coefficients between pH values and element content in soil (Table 4).

Table 4

Correlation coefficient between pH and contents of the analyzed trace elements in soil

Zn			Cu			Ni			Cr		
I	II	III	I	II	III	I	II	III	I	II	III
–0.13	0.68*	–0.42	0.15	–0.17	0.29	–0.20	0.75*	0.40	0.28	0.20	0.78*
Cd			Pb			Fe			Mn		
I	II	III	I	II	III	I	II	III	I	II	III
–0.41	–0.63*	–0.51	–0.60	–0.66*	–0.26	0.28	–0.54	0.45	–0.06	–0.51	0.04

I – total content, II – 0.01 mol $CaCl_2 \cdot dm^{-3}$, III – 1 mol $HCl \cdot dm^{-3}$, * r significant $p < 0.05$.

In conclusion, applied bottom deposit revealed in its composition a considerable share of silt and clay fractions, alkaline reaction and low total heavy metal content, therefore it may be applied as an admixture to light soils to improve their productivity. The experiment demonstrated that the applied bottom deposit supplement positively affected improvement of the analyzed soil and decreased both total and available content of elements toxic for plants, ie lead and cadmium. Moreover, as reported by Pelczar et al [6] bottom deposits may be used for reclamation of mining wastes. The authors revealed that adding bottom deposit to mining wastes changes their buffer properties, porosity and capability for water retention, increases the contents of organic substance, fertilizer components and causes an increase in enzymatic activity of soil.

Conclusions

1. A positive effect of bottom deposit on the increase in light soil pH value was revealed. After a two-year period of research light soil pH value was 6.24 on the control treatment, 6.49 on the treatment with a 5 % sediment supplement and 6.86 on the treatment with a 10 % deposit admixture.

2. Bottom deposit supplement to the light soil significantly diminished the contents of available forms of zinc, lead and manganese extracted with 1 mol $HCl \cdot dm^{-3}$ and bioavailable forms of cadmium, lead, manganese and iron extracted with 0.01 mol $CaCl_2 \cdot dm^{-3}$.

3. The experiment did not reveal any significant effect of the soil pH on diminished availability of most analyzed elements as it has been confirmed by negative and insignificant values of correlation coefficients between pH and element content in soil.

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WPŁYW DODATKU OSADU DENNEGO NA ZAWARTOŚĆ PIERWIASTKÓW ŚLADOWYCH W GLEBIE LEKKIEJ

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Abstrakt: Celem badań była ocena wpływu dodatku osadu dennego na zawartość i mobilności wybranych pierwiastków śladowych w glebie lekkiej. W badaniach wykazano dodatni wpływ osadu dennego na zwiększenie wartości pH gleby lekkiej. Po 2-letnim okresie badań wartość pH gleby wyniosła: 6,24 w obiekcie kontrolnym, 6,49 w obiekcie z 5 % dodatkiem osadu i 6,86 w obiekcie z 10 % dodatkiem osadu dennego. Dodatek osadu dennego do gleby lekkiej zmniejszył znacznie zawartość form przyswajalnych cynku, ołowiu, i manganu ekstrahowanych 1 mol HCl $\cdot$ dm^{-3} oraz biodostępnych kadmu, ołowiu, manganu i żelaza ekstrahowanych 0,01 mol $CaCl_2$ $\cdot$ dm^{-3}. W badaniach nie stwierdzono istotnego wpływu odczynu gleby na zmniejszenie dostępności większości badanych pierwiastków, potwierdzeniem tego są ujemne i statystycznie nieistotne wartości współczynników korelacji pomiędzy wartością pH a zawartością pierwiastków w glebie.

Słowa kluczowe: osad denny, pierwiastki śladowe, gleba lekka, wyciągi: 0,01 mol $CaCl_2$, 1 mol HCl $\cdot$ dm^{-3}

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DEGRADATION PROCESSES IN DIFFERENTLY USED LOESS SOILS OF SOUTHERN POLAND

PROCESY DEGRADACJI W RÓŻNIE UŻYTKOWANYCH GLEBACH LESSOWYCH POŁUDNIOWEJ POLSKI

Abstract: The processes of soil degradation present a serious threat to ecosystem sustainability. The objectives of the work were: to estimate differences in microstructures of loess soils of agro-, meadow and deciduous forest ecosystems, and to evaluate the extent to which image analysis could be applied to measure changes in this property. The arable soil was characterized by a lower value of macroporosity and the image area occupied by organic matter aggregates while meadow soil with a high amount of organic matter and neutral soil reaction presented the highest share of large excrements attributed to earthworms. Results of this work confirm opinions that deep tillage compaction can reduce the biomass and diversity of most soil organisms while hay crops improves soil fertility and helps maintaining biodiversity. The image analysis protocols developed to quantify the soil features mostly affected by the way of soil use, resulted effectively in bringing out differences between those properties in analyzed soils.

Keywords: arable, meadow, forest, loess soils, aggregation, porosity, micromophometric analyses

The processes of soil degradation present a serious threat to biomass, crop yields and ecosystem sustainability. Therefore, they must be controlled and the main aim of land management should be the reduction of the environmental impact of agricultural practices [1–3]. A way to evaluate the impact of management practices on the soil environment is to quantify the accumulation and decomposition of organic matter, soil fauna activity, aggregation and porosity. Soil aggregation has a great influence on its physical characteristics. Well aggregated soils possess a larger pore space and a higher infiltration rate leading to enhanced microbial activity in comparison with poorly aggregated one. Aggregates are also thought to play an important role in the protection of soil organic matter. The preservation of soil organic matter is desirable for land use as it is a key component in nutrient cycling. Furthermore, the retention of organic C in

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soil is becoming more important since the rise in atmospheric CO_2 and global climate warming have become recent concerns [4, 5]. A decisive role in the formation and stability of macro- and microaggregates play the activity of earthworms and other soil fauna representatives by removing plant litter and other organic materials from the soil surface and their incorporation into soil aggregates. Much of the environmental damage in arable lands such as erosion or susceptibility to compaction originate from soil structure degradation, which can be quantified by measurements of pore space, size, shape and continuity [6, 7].

Soils derived from loess have generally high natural fertility and productivity. Fertility of loess soils depends upon their large available water capacities, good aeration, ease of cultivation and moderately large reserves of most mineral nutrients. Properties of loess soils contrast clearly with typical poor, acid sandy soils that cover the major part of Polish territory. Therefore, loess soils have been submitted to the excessive long-lasting agricultural practices, which together with often inappropriate agro-technological treatment have resulted in their degradation [8, 9].

The objectives of the work were: (i) to estimate differences in microstructures, porosity and faunal activity of loess soils of agro-, meadow and deciduous forest ecosystems, and (ii) to evaluate on thin sections the extent to which image analysis could be applied to measure changes in void space, structure and excrement features related to degradation processes.

Materials and methods

Studies were carried out on the southern part of Proszowice Plateau which belongs to Malopolska Upland (50^o 06′ N and 20^o 20′ E) in southern Poland. The area is situated at the altitude of 300 m a.s.l. and formed from Miocene deposits covered with loess originating from the Baltic glaciations. Mean annual temperature ranges from 7.5 to 8 ^oC and the growing season lasts 210–220 days [8].

Soil samples were collected in September 2007 from three areas representing arable, meadow and forest soils, classified according to WRB classification, as chernozems. All studied soils had texture of silt with the content of sand, silt and clay ranged between 9–11 %, 73–76 % and 13–15 %, respectively. On arable soils wheat was cultivated, meadow soil was covered with grassland community belonging to *Arrhenatheretalia* association, and the forest soil was overgrown with deciduous forest from *Querco-Fagetalia* association.

Soil samples were taken from every type of land use from three outcrops. They were sampled from 2 horizons: surface (0–25 cm) and subsurface (25–40 cm) to perform chemical analyses. From every site and every studied soil horizon undisturbed soil samples for micomorphometric analyses were also collected.

For chemical analyses soil samples were air dried and sieved through 2 mm mesh sieve. In samples prepared in this way pH in 0.01 mol · dm^{-3} $CaCl_2$ was measured potentiometrically, while organic carbon and total nitrogen with the use of automatic C and N analyzer: TOC-TN 1200 Thermo Euroglas apparatus.

Undisturbed soil samples (4 × 6 × 3 cm) were impregnated with Araldite resin under vacuum conditions, in Epovac apparatus and cut and grind to 40 μm thick slices. Observations of soil thin sections were conducted using Nicon Eclipse E400 POL polarizing microscope in light passing through parallel nicols, using magnifications of 20×. Three representative areas of each slide were subjected to micromorphometric analysis using Aphelion ADCIS S.A., Aai Inc programme. Every analyzed image was divided into areas occupied by pores, plant rests and organic aggregates by color thresholding. For identified features, data on percent area coverage and size parameters were extracted. The classification of excrements was based on descriptions found in Bullock et al [10].

All the analyses were performed in three replicates. The results were subjected to unifactor STATISTICA 8, ANOVA analysis and a posteriori Fisher's test was used to study a significance of differences between studied objects at significance level 0.05. Simple correlation coefficients (r) between selected soil properties were calculated. A significance of correlation coefficients was estimated with the use of t-Student test.

Results and discussion

The mean level of organic carbon in top horizons of arable soils was twofold lower than in respective horizons of meadow soils and 4.5-fold lower than in top horizons of forest soils (Table 1). According to Bronick and Lal [3], differences in organic carbon contents between cultivated soils and analogical soils of natural ecosystems can amount to 25–75 %. They result from the decrease of biomass returning to soil and the increase of mineralization rate related with changes of soil moisture. Additionally cultivated soils are much more susceptible to erosion and nutrients leaching than soils of natural ecosystems. Studied arable soils were characterized by a low C:N ratios (Table 1) which indicate more intensive humus mineralization in these soils than in meadow and forest ones. As a result of these processes a large amounts of organic carbon in form of CO_2 volatilize out of soil simultaneously decreasing carbon sequestration in the soil [3]. In all studied profiles pH values were higher in subsurface horizons than in surface ones (Table 1). It resulted from leaching of carbonates with rainfall water and enhanced additionally in arable soils by acidifying effect of chemical fertilizers and in forest soils by forest vegetation.

Table 1

Selected physico-chemical properties of upper horizons of studied soils

Soil use	Horizon	Depth of soil horizons [cm]	pH 0.01 mol · dm^{-3} $CaCl_2$	$C_{org.}$	$N_{tot.}$	C:N
				[g · kg^{-1}]		
Arable	A1	0–25	5.8	32.1	3.4	9.5
	A2	25–40	6.1	21.6	2.4	8.9
Meadow	M1	0–25	6.1	46.7	3.9	12.1
	M2	25–40	6.4	24.2	2.3	10.3
Forest	F1	0–25	5.6	65.7	4.2	15.7
	F2	25–40	5.9	9.5	0.8	11.9

As expected the lowest amounts of plant rests were found in both horizons of arable soils and the highest in the top horizon of forest soil (Fig. 1). The last fact is related with the type of forest vegetation rich in lignin and cellulose, characterized by the low rate of decomposition, which is considered a key factor in carbon turnover rates, enhancing aggregation. The amount of plant fragments reflects C:N ratio as both values express the intensity of mineralization processes going through in soils. Therefore, the higher value of C:N is in the studied soil the larger area of image is occupied by plants rests, with a simple correlation coefficient between discussed parameters amounted to 0.954 significant at $p \leq 0.001$. This high correlation between these amounts proves the usefulness of micromophometric methods for the good explanation of the discussed soil phenomena.

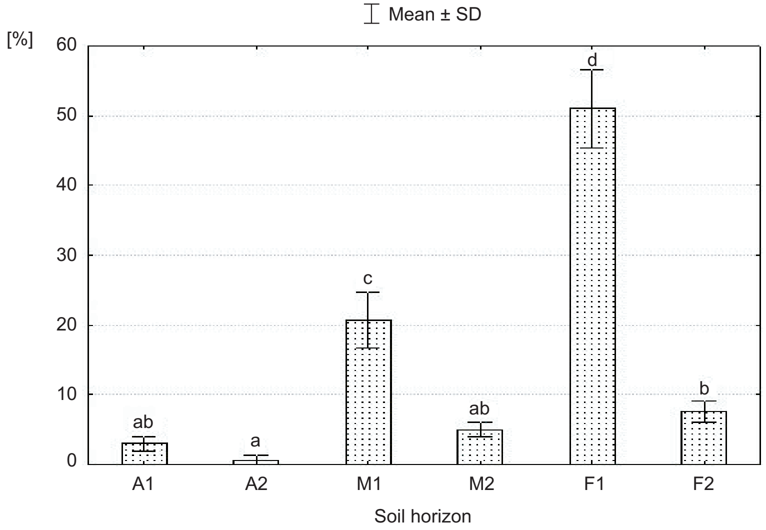

Fig. 1. Share of plants rests in the total image area in surface and subsurface horizons of studied soils (Indications of soil horizons are given in Table 1, the same letters above columns indicate a lack of statistically significant differences at the significance level ≤ 0.05)

Figure 2 shows the share of organic matter aggregates in the total image area of surface and subsurface horizons of studied arable, meadow and forest soils. It illustrates significant differences in this value between studied horizons. The largest image area occupied by organic matter aggregates was determined in the top horizon of meadow soil, a bit smaller in analogical horizon of forest soil and significantly smaller in horizons of arable soil. At the same time, it should be emphasized that the area occupied by aggregates was distinctly lower in subsurface horizon of arable soil than in top horizon of that soil. The fact indicates deterioration in the quality of soil structure, and in consequence reduction of soil functions. The organic particles area is associated with the content of organic carbon. Simple correlation coefficient (r) counted between soil aggregation area and the content of organic carbon amounted to 0.614 significant at $p \leq 0.001$.

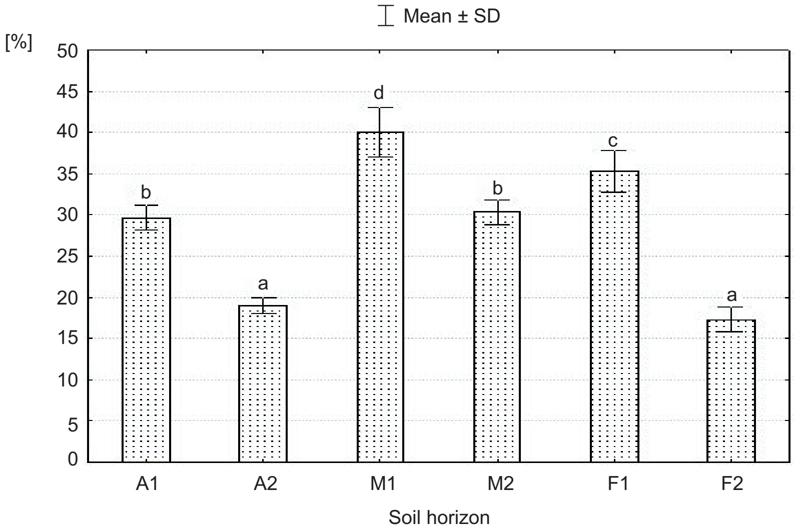

Fig. 2. Share of organic matter aggregates in the total image area in surface and subsurface horizons of studied soils (Explanations in Fig. 1)

The aggregates observed in thin sections were predominantly of faunal origin. According to thin section observations and considering size of aggregates related to their distinctive morphologies 3 classes of excrements were set: with the diameter less than 50 μm, between 50 and 300 μm and bigger than 300 μm. The smallest aggregates comprised three types: organic spheroids within root and plant fragments attributed to *Oribatid* mites, occurring mainly in top horizons of forest soils, irregular ellipsoids of amorphous organic material interpreted as derived from small *Collembola* species, occurring in all top horizons but prevailing in meadow soils and undifferentiated fused or aged excrements, found mostly in top horizons of arable soil. Among the medium large aggregates there were irregular spheroids of organic material attributed to *Enchytraeids*, found mostly in forest soils, *Collembola* excrements occurring in all studied soils and regular ellipsoids within plant fragments identified as *Diptera* larvae excrements, numerous in meadow soils. Aggregates of diameter larger than 300 μm were mainly of Earthworm's origin. They were in shape of mammilated organic or organic mineral excrement's or vermiform structure. They were present in all soils but with clear prevalence in meadow soil.

Figure 3 presents the percentage of aggregates of given size in the total aggregation. Results indicated that meadow soil with a high amount of organic matter and neutral soil reaction presented higher share of large excrements attributed to earthworms than forest or arable soils. Forest soils are generally attractive to earthworms only after some weathering and degradation of fresh deciduous litter by fungi and bacteria and in a small presence of earthworms numerous *Enchytraeids* aggregates were noticed there. Results of this work confirm also opinions of many authors [2–4, 11] that deep tillage compaction can reduce the biomass and diversity of most soil organisms while hay crops improves soil fertility and helps maintaining biodiversity. Intensification of

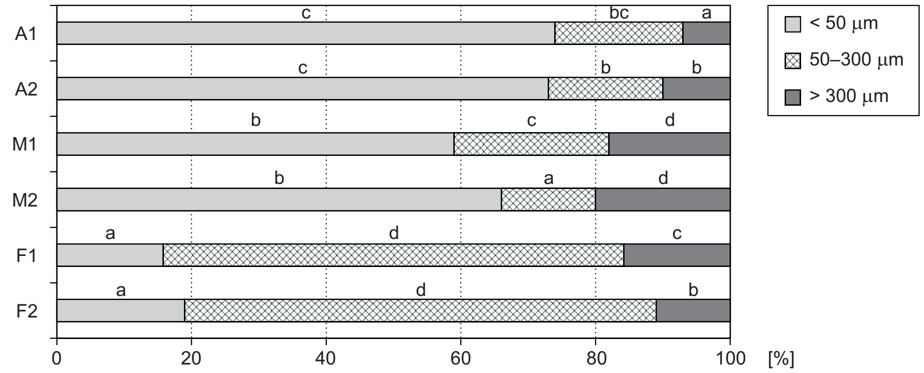

Fig. 3. Share of faunal aggregates with different diameters in the total aggregation in surface and subsurface horizons of studied soils (Explanations in Fig. 1)

cropping, annual tillage and other operations such as fertilization or pesticide use consistently affect populations of earthworms and other invertebrates. As a consequence they lead to modification of soil physical properties resulting in damage to soil structure.

The share of macropores (pores larger than 50 μm in diameter) in studied soil surface and subsurface horizons is presented in Fig. 4. Results show that according to the micromorphometric method [2], almost all studied soil horizons were moderately porous as they porosity ranges from 10 % to 25 %. Nevertheless statistically significant differences were calculated between their macroporosity. The highest value of macroporosity were determined in a top horizon of meadow soil and subsurface horizon of forest soil, while significantly lower values characterized the top horizon of arable soil.

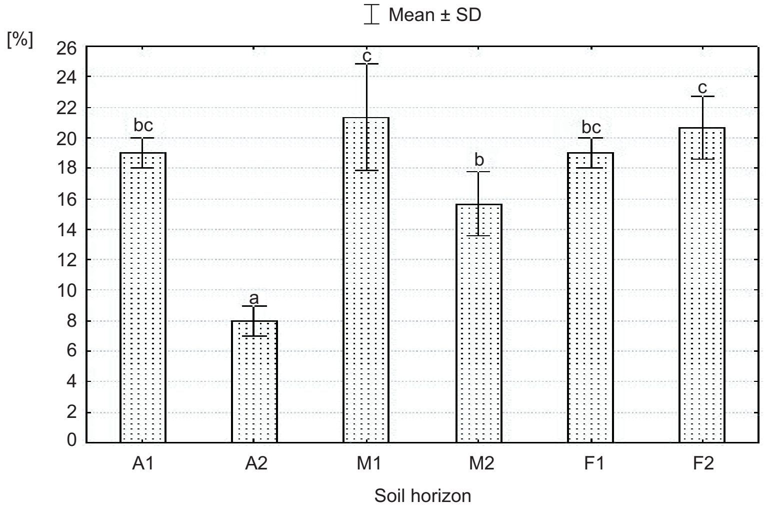

Fig. 4. Share of macroporosity in the total image area in surface and subsurface horizons of studied soils (Explanations in Fig. 1)

The lowest value of the total macroporosity (< 10 %), was found in the subsurface horizon of the arable soil which placed that soil layer among dense soils.

For a more detailed characterization of soil pores, pore size distribution was also counted with a special attention given to pores of diameter ranging from 50 to 500 μm (Fig. 5). This group of pores, according to Pagliai et al [2], is formed by transmission pores, which are important in soil–water–plant relationships and in maintaining good soil structure conditions. Therefore, damage to soil structure can be recognized by a decrease in the share of transmission pores. Figure 5 shows that shares of both transmission and large pores were significantly lower in studied horizons of arable soil than in horizons of meadow and forest soils. The highest shares of transmission pores were in both studied horizons of forest soil while the biggest part of large pores was determined in horizons of meadow soil. The results of this study validated that ploughing and other agricultural practices performed in arable soil induced decrease of porosity, in particular of the transmission and large pores. The negative aspects associated with this phenomenon could be the formation of ploughpan at the lower cultivation limit, which besides a reduction of water movement, may also hamper root growth.

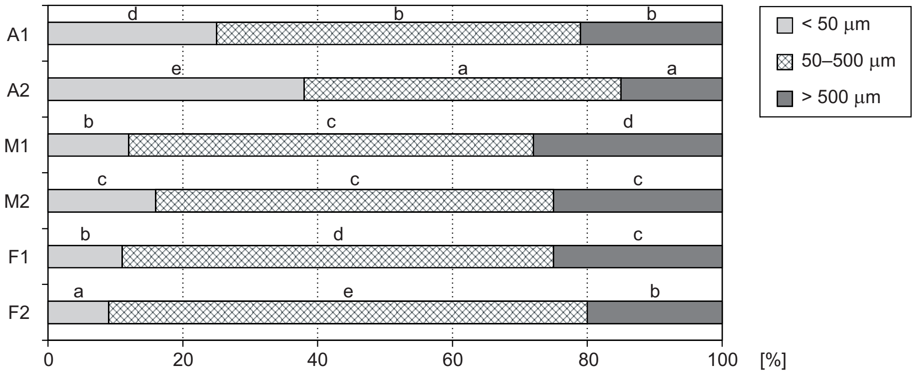

Fig. 5. Share of voids with different diameters in the total porosity in surface and subsurface horizons of studied soils (Explanations in Fig. 1)

Conclusions

1. Among forest, meadow and arable soils signs of degradation resulting from the use of soil and expressed by a decrease in soil organic matter content, porosity, aggregation and faunal activity were the most pronounced in the arable soil and the least in the meadow one.

2. Differences in soil properties between the three ways of soil use were not as distinct to be alarmed as the negative impact on soil structure exercised by agricultural practices was hampered by the beneficial effect of secondary carbonates which enhanced soil aggregation.

3. The image analysis protocols developed to quantify aggregation, void space and distribution, as the soil features mostly affected by the mode of soil use, resulted effective in bringing out differences between those properties in analyzed soils.

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PROCESY DEGRADACJI W GLEBACH LESSOWYCH W POŁUDNIOWEJ POLSCE

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Abstrakt: Procesy degradacji stanowią duże zagrożenie dla stabilności ekosystemów. Celami pracy było: ustalenie różnic w mikrostrukturze gleb lessowych ekosystemów uprawnych, łąkowych i lasów liściastych oraz określenie w jakim stopniu analiza obrazu może być stosowana do określania zmian tej właściwości. Gleba orna charakteryzowała się najniższą mikroporowatością i powierzchnią obrazu zajmowaną przez agregaty materii organicznej pochodzenia zwierzęcego, podczas gdy w glebie łąki, w której oznaczono dużą zawartość materii organicznej i obojętny odczyn, występował również największy udział dużych ekskrementów przypisywanych dżdżownicom. Rezultaty tej pracy potwierdzają opinie, że orka powodująca kompakcję gleby może redukować biomasę i różnorodność organizmów glebowych, podczas gdy użytkowanie łąkowe pomaga w utrzymaniu bioróżnorodności. Metody analizy obrazu stosowane do określania jakości właściwości gleb, modyfikowanych głównie poprzez sposób użytkowania okazały się skuteczne dla określenia różnic w tych właściwościach między analizowanymi glebami.

Słowa kluczowe: ekosystemy orne, łąkowe, lasów liściastych, gleby lessowe, agregatowość, porowatość, analizy mikromorfometryczne

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Janina GOSPODAREK[1] and Aleksandra NADGÓRSKA-SOCHA[2]

EFFECT OF SOIL CONTAMINATION WITH HEAVY METALS IN A MIXTURE WITH ZINC AND NICKEL ON THEIR CONTENT IN BROAD BEAN (*Vicia faba* L.) ROOTS AND SHOOTS

WPŁYW SKAŻENIA GLEBY METALAMI CIĘŻKIMI W MIESZANINIE Z CYNKIEM I NIKLEM NA ICH ZAWARTOŚĆ W KORZENIACH I PĘDACH BOBU (*Vicia faba* L.)

Abstract: The research aimed at an assessment of soil contamination with mixtures of heavy metals (Pb, Cu and Cd) with zinc and nickel on two levels of pollution on heavy metal concentrations in broad bean roots and shoots. The contents of individual analyzed metals in broad bean were diversified and dependant on both the examined plant part and the kind of accompanying metal. Soil contamination with mixtures of cadmium or copper with zinc on a higher level of pollution leads to their highest concentrations in broad beans. On the other hand, the highest lead concentrations were assessed when broad bean was cultivated in the soil contaminated with a mixture of this element with nickel on a higher level of pollution. A considerable differentiation in zinc and nickel uptake by broad bean plants dependant on the kind of accompanying metal was found. The highest zinc concentration in roots was assessed when broad bean was cultivated in the soil contaminated with a mixture of this element with lead on a higher level of pollution, whereas in the aboveground parts when Zn was used in the mixture with cadmium. The highest concentration of nickel was detected in broad bean roots grown in the soil contaminated with this metal mixed with copper, whereas in the aerial parts Ni content was greatest when soil was polluted with a mixture of nickel and zinc.

Keywords: mixtures of heavy metals, soil pollution, *Vicia faba* L.

Soil contamination by a joint dose of heavy metals often reveal a different effect on growth and development of plants than when metals occurring singly [1]. Also heavy metal concentrations in plant may differ because of their potential mutual antagonistic

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or synergistic effect [2, 3]. Previous investigations demonstrated that among five heavy metals (Zn, Ni, Cu, Pb and Cd) zinc and nickel had the strongest (negative) effect on broad bean plant growth.

The work aimed at an assessment of soil contamination with mixtures of heavy metals (Pb, Cu and Cd) with zinc and nickel on two levels of pollution on heavy metal concentrations in broad bean plants.

Material and methods

Broad bean, White Windsor c.v. was cultivated in a control soil with natural heavy metal concentrations and in the soil contaminated with mixtures of heavy metals or with single metals (Table 1).

Table 1

Experimental design

Treatments	Cd dose [mg · kg^{-1} d.m.]	Cu dose [mg · kg^{-1} d.m.]	Pb dose [mg · kg^{-1} d.m.]	Ni dose [mg · kg^{-1} d.m.]	Zn dose [mg · kg^{-1} d.m.]
Control (C)	—	—	—	—	—
C+NPK	—	—	—	—	—
Control (1)	—	—	—	—	—
C+NPK (1)	—	—	—	—	—
ZnII+CdII	2.25	—	—	—	350
ZnIII+CdIII	4	—	—	—	1000
ZnII+CuII	—	65	—	—	350
ZnIII+CuIII	—	85	—	—	1000
ZnII+PbII	—	—	175	—	350
ZnIII+PbIII	—	—	530	—	1000
NiII+ZnII	—	—	—	62.5	350
NiIII+ZnIII	—	—	—	110	1000
NiII+CdII	2.25	—	—	62.5	—
NiIII + CdIII	4	—	—	110	—
NiII+CuII	—	65	—	62.5	—
NiIII+CuIII	—	85	—	110	—
NiII+PbII	—	—	175	62.5	—
NiIII+PbIII	—	—	530	110	—
CdIII (1)*	4	—	—	—	—
CuIII (1)	—	85	—	—	—
PbIII (1)	—	—	530	—	—
NiIII (1)	—	—	—	110	—
ZnIII (1)	—	—	—	—	1000

* The (1) means the soil, which was polluted and used last year (2007).

The level of soil contamination corresponded to II and III class of pollution acc. to the classification suggested by IUNG in Pulawy [4]. The plants were cultivated in plastic pots with 9.8 kg d.m. of soil under field conditions. Detailed description of the methods of heavy metal supply into the soil was presented in another publication [5]. Mineral fertilization, the same on all objects (except for the non-fertilized control), dosed: 0.7 g N (in NH_4NO_3); 0.8 g P_2O_5 (in KH_2PO_4); 1.2 g K_2O (in KCl) per pot was applied simultaneously with heavy metal addition to the soil. In the objects where a $Pb(NO_3)_2$ supplement was added a certain amount of nitrogen was also added to the soil, its dose was relatively diminished in the basic fertilization. The experiment was conducted in 2008 on degraded chernozem developed from loess with acid reaction (pH in 1 mol $\cdot$ dm^{-3} KCl solution was 5.5 and in water 6.3) and organic carbon content 1.13 %. On objects where the soil was contaminated with single heavy metals, the soil polluted in the previous year, in which also broad bean was cultivated in 2007, was used.

Samples for chemical analyses were collected at milk ripeness of seeds. Chemical analysis of the plant material comprised an assessment of heavy metal concentrations (cadmium, lead, zinc, copper and nickel). Plant material was washed in tap and in distilled water, dried in 105 ^{o}C to a constant weight and ground to fine powder, then mineralized and dissolved in 10 % HNO_3. After filtration: Zn, Pb, Ni, Cu and Cd content was measured using Flame Atomic Absorption Spectrometry (AAS) [6, 7]. The quality of the analytical procedure was controlled by using samples of the reference material in each series of analysis (Certified Reference material CTA-OTL-1 Oriental Tobacco Leaves). The data were processed using software Statistica to compute significant statistical differences between samples ($p < 0,05$) according to Tukey's multiple range test.

Results and discussion

With a lapse of time from the moment of soil pollution heavy metals may undergo various changes conditioned by the soil physico-chemical properties, the weather or specific biogeochemical characteristics of individual elements. Their content does not always diminish proportionately to the passage of time. The experiment compared the results obtained for the mixtures with the results from the object where metals were applied singly but a year before. The Authors' research on heavy metal contents in broad bean in time elapsing from the moment of pollution demonstrated that cadmium concentration in plants was not decreasing even 3 years after pollution. Cu and Pb contents were declining a year after contamination but only in the aboveground parts. On the other hand, Zn and Ni levels were decreasing in plants only 2 years after the moment of contamination [8].

The highest zinc concentrations in broad bean shoots was assessed when it was grown in the soil contaminated only with zinc. Application of this metal in a mixture with all other elements contributed to a significant lowering of zinc content in broad bean shoots (Fig. 1A). The effect was the weakest when a mixture of zinc and cadmium was used while the strongest when the soil was contaminated with a mixture of zinc and nickel. It was similar for broad bean cultivated in the soil contaminated with the above – mentioned metal mixtures on a lower level of pollution. Also in this case the lowest zinc concentration was registered in broad bean shoots when the element was used in a mixture with nickel. The underground broad bean parts revealed the highest zinc concentrations in the soil polluted with this element mixed with lead on a higher level. On the other hand, broad bean roots had the smallest amounts of zinc when cultivated in a mixture with copper (Fig. 1B). Application of zinc in mixtures with individual tested heavy metals on a lower level did not cause any major changes in this metal concentrations in broad bean roots.

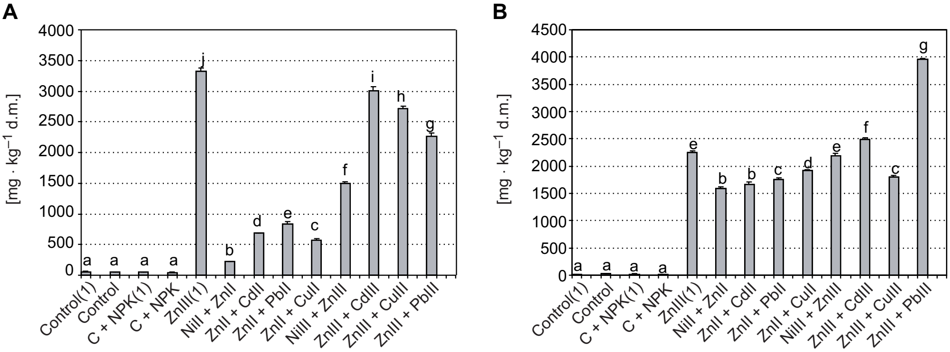

Fig. 1. Zinc content in shoots (A) and roots (B) of broad bean (*Vicia faba* L.) cultivated in unpolluted soil (Control, C + NPK) and in soil contaminated with heavy metals. The (1) means the soil, which was polluted and used last year (2007). Values marked with different letters are statistically different at $p < 0.05$.

Nickel content in broad bean shoots increased when the plant was cultivated in the soil contaminated with a mixture of this metal with zinc on a higher level. It was ca 20 % higher in comparison with the object where broad bean was grown in the soil contaminated only with nickel. On the other hand, the use of the same Ni dose but in mixtures with Cd, Cu or Pb was causing almost three-fold decline in broad bean shoot nickel concentrations (Fig. 2A). Soil contamination with mixtures of Ni and the other analyzed metals in lower doses caused ca 20-fold increase in this metal content in broad bean shoots in comparison with the control plants, irrespective of the kind of applied mixture. Nickel concentrations in broad bean roots looked different (Fig. 2B). The

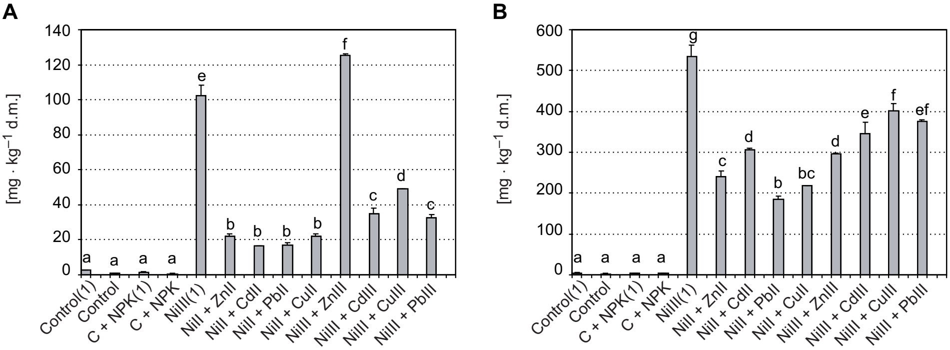

Fig. 2. Nickel content in shoots (A) and roots (B) of broad bean (*Vicia faba* L.) cultivated in unpolluted soil (Control, C + NPK) and in soil contaminated with heavy metals The (1) means the soil, which was polluted and used last year (2007). Values marked with different letters are statistically different at $p < 0.05$.

highest contents were assessed in broad bean roots grown in the soil contaminated only with nickel. Nickel applied in the same dose but mixed with the other metals caused that this element content in broad bean roots was lower (by ca 25–45 %). Soil contamination with a lower dose of heavy metals caused an increase in Ni content from ca 48-fold, (in comparison with the control) when used in a mixture with lead, to ca 80-fold when the soil was polluted with a mixture of Ni and Cd.

Like in the case of nickel, also Cu content in broad bean shoots increased most when the plant was cultivated in the soil contaminated with this metal mixture with Zn (in a higher dose). On the other hand, Cu level in broad bean shoots grown in the soil contaminated with this metal mixed with Ni on a higher level and Ni or Zn on a lower level, was similar to the contents in the control plants (Fig. 3A). On the other hand, in roots the soil contamination with all analyzed metals on both levels caused a significant increase in Cu content, which was the strongest when the metal was applied singly (Fig. 3B). In the case of mixtures Zn company more than Ni favoured an increase in Cu level in roots.

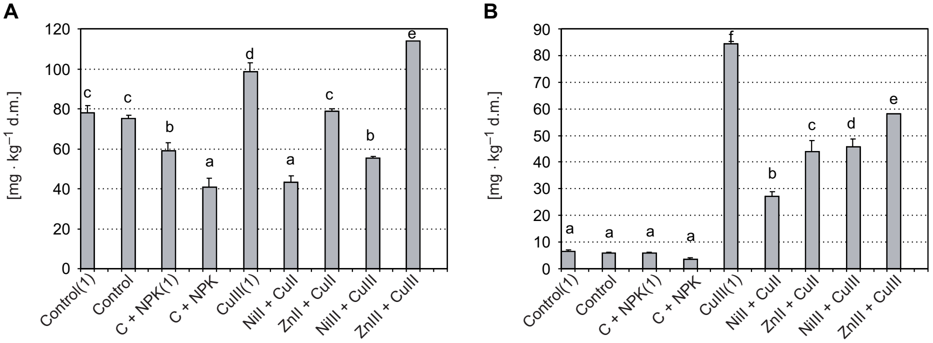

Fig. 3. Copper content in shoots (A) and roots (B) of broad bean (*Vicia faba* L.) cultivated in unpolluted soil (Control, C + NPK) and in soil contaminated with heavy metals The (1) means the soil, which was polluted and used last year (2007). Values marked with different letters are statistically different at $p < 0.05$.

Like in case of Cu and Ni, also Cd application in a mixture with Zn favoured its uptake by the plant and increase in its shoots concentrations more than when it was used in a mixture with Ni and more than when applied as a single metal (Fig. 4A). A possible cause might have been a usual greater decrease in the soil pH accompanying the soil zinc contamination as compared with nickel pollution [9]. On the other hand, cadmium content in roots was the highest in plants cultivated in the soil contaminated with this metal used singly. From among the mixtures applied in higher doses, zinc combined with cadmium favoured Cd uptake more than nickel (Fig. 4B). Various elements differently affect cadmium accumulation by plants. Copper and zinc decrease cadmium amount in plants, whereas lead increases its concentration [10].

Broad bean shoots cultivated in the soil contaminated solely with lead revealed the highest concentrations of this element. An admixture of zinc or nickel contributed to a decline in lead concentrations in broad bean shoots (Fig. 5A). On the other hand

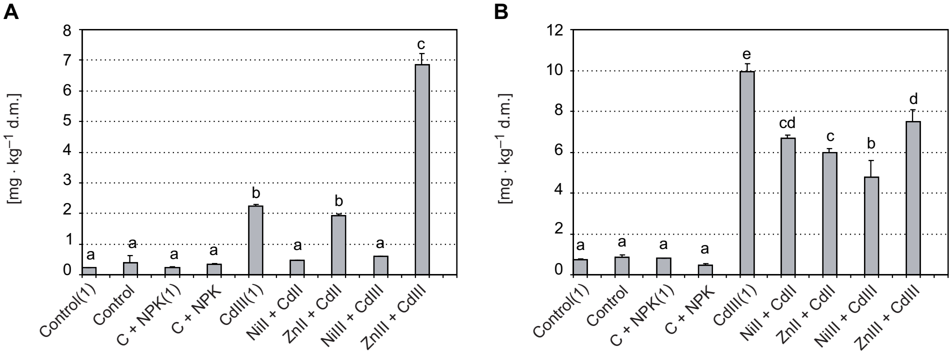

Fig. 4. Cadmium content in shoots (A) and roots (B) of broad bean (*Vicia faba* L.) cultivated in unpolluted soil (Control, C + NPK) and in soil contaminated with heavy metals The (1) means the soil, which was polluted and used last year (2007). Values marked with different letters are statistically different at $p < 0.05$.

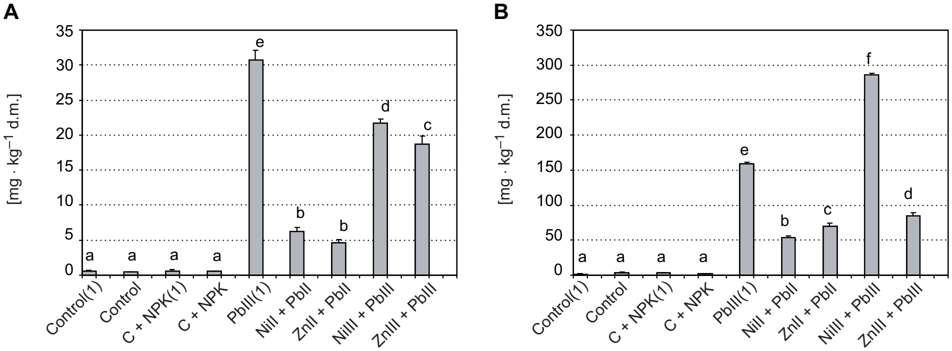

Fig. 5. Lead content in shoots (A) and roots (B) of broad bean (*Vicia faba* L.) cultivated in unpolluted soil (Control, C + NPK) and in soil contaminated with heavy metals. The (1) means the soil, which was polluted and used last year (2007). Values marked with different letters are statistically different at $p < 0.05$.

broad bean roots contained the highest amounts of Pb when it was grown in the soil contaminated with this metal mixture with Ni on a higher level. Applied mixtures of lead and zinc on a higher level resulted in ca three-fold decline in Pb content in broad bean roots in comparison with the soil polluted with a mixture of Ni and Pb in a higher dose and about 2-fold decrease as compared with the object where the soil was polluted only with Pb (Fig. 5B). Zinc causes disturbances in lead transport to plant aerial parts [11].

Conclusions

1. The contents of individual analyzed metals in broad bean were diversified and dependant on both the examined plant part and the kind of accompanying metal.

2. Soil contamination with mixtures of cadmium or copper with zinc on a higher level of pollution leads to their highest concentrations in broad beans. On the other hand, the highest lead concentrations were assessed when broad bean was cultivated in the soil contaminated with a mixture of this element with nickel on a higher level of pollution.

3. A considerable differentiation in zinc and nickel uptake by broad bean plants dependant on the kind of accompanying metal was found. The highest zinc concentration in roots was assessed when broad bean was cultivated in the soil contaminated with a mixture of this element with lead on a higher level of pollution, whereas in the aboveground parts when Zn was used in the mixture with cadmium. The highest concentration of nickel was detected in broad bean roots grown in the soil contaminated with this metal mixed with copper, whereas in the aerial parts Ni content was greatest when soil was polluted with a mixture of nickel and zinc.

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WPŁYW SKAŻENIA GLEBY METALAMI CIĘŻKIMI W MIESZANINIE Z CYNKIEM I NIKLEM NA ICH ZAWARTOŚĆ W KORZENIACH I PĘDACH BOBU (*Vicia faba* L.)

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Abstrakt: Celem pracy było określenie wpływu skażenia gleby mieszaninami metali ciężkich z cynkiem i niklem na dwóch poziomach zanieczyszczenia na ich zawartość w roślinach bobu. Poziom skażenia gleby odpowiadał II i III klasie zanieczyszczenia gleb według klasyfikacji opracowanej przez IUNG w Puławach.

Zawartość poszczególnych badanych metali w bobie była zróżnicowana i uzależniona zarówno od części badanej rośliny, jak i rodzaju metalu towarzyszącego. Skażenie gleby mieszaninami kadmu lub miedzi z cynkiem na wyższym poziomie zanieczyszczenia prowadzi do największej koncentracji ww. metali w bobie. Natomiast najwyższą zawartość ołowiu stwierdzono, gdy bób był uprawiany w glebie skażonej mieszaniną tego pierwiastka z niklem na wyższym poziomie zanieczyszczenia. Stwierdzono znaczne zróżnicowanie w pobieraniu cynku i niklu przez rośliny bobu zależnie od rodzaju metalu towarzyszącego. Największą koncentrację cynku w korzeniach stwierdzono, gdy bób był uprawiany w glebie skażonej mieszaniną tego pierwiastka z ołowiem na wyższym poziomie, natomiast w częściach nadziemnych w mieszaninie z kadmem. Największą koncentracją niklu charakteryzowały się korzenie bobu uprawianego w glebie skażonej tym metalem w mieszaninie z miedzią, natomiast części nadziemne w mieszaninie niklu z cynkiem.

Słowa kluczowe: mieszaniny metali ciężkich, zanieczyszczenie gleby, *Vicia faba* L.

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Bogdan KULIG[1]

ABIOTIC FACTORS IN CROP MODELS

CZYNNIKI ABIOTYCZNE W MODELACH ROŚLINNYCH

Abstract: Dynamic development of models describing growth, development and yielding of plants was observed in the last quarter of the 20th century. Explanatory models interpreting the phenomena constitute a specific group. Modeling of biomass accumulation is most frequently presented on three levels of productivity: potential, limited by the access to water and minerals and obtainable (reduced by the presence of weeds, diseases and pests). Modeling provides plenty of valuable information for proper interpretation and better understanding of the investigated process. Knowledge obtained in this way may be used to conduct so called simulation experiments using models, which can be of particular importance for research on the protection of the natural environment (eg migration and transformation of pesticides, biogens or heavy metals in soil).

Keywords: crop models, abiotic factors

The quantity of biomass accumulated by the canopy is the effect of a complex of meteorological and soil factors, ecophysiological plant properties of various degrees of importance and differently interconnected. It is an exceptionally complicated process and difficult to quantify. Still, owing to the development of electronic computational techniques in the last quarter of the 20th century, a dynamic evolution of models describing plant growth, development and yielding occurred. Explanatory (mechanistic) models interpreting the mechanisms of the phenomenon constitute a particular group. Determining the formula of the function describing a model requires theoretical knowledge about the course of a phenomenon usually using the laws of physics, chemistry or physiology [1, 2].

Due to universal applications of simulation models in agricultural sciences they may be divided into:

– models of physical, chemical and biological processes (eg water flow in a soil profile or erosion process modeling, etc.)

– models describing comprehensively a single plant species growth and development (eg Oryza, Ceres-Maize),

– models describing comprehensively the growth and development of many plant species (SUCROS, WOFOST, DSSAT, APSIM, EuroACCES and others),

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– systems of models analysing the situation on various levels of production system organization and in different time and space scales – ALMANAC, MARS-CGMS, IMPEL [1–4].

It should be stated that the impact of abiotic factors on plants may be regarded on different levels. Field research (canopy) and pot experiments (single plant) try to estimate the quantitative and qualitative effect of abiotic and biotic factors on the amount of accumulated biomass and usable yield. Currently, interdisciplinary research aimed at the identification of the mechanism or plant response to stressors on cell levels has been frequently conducted by plant physiologists, geneticists and biochemists [5].

The role of abiotic factors on an example of selected crop models

Modeling of biomass accumulation is most frequently presented on three levels of productivity:

1. potential production – with determining factors, such as solar radiation, temperature, CO_2 concentration and plant genetic traits,
2. attainable production – with limiting factors – water and mineral supply,
3. actual (reduced) production with reducing factors – weeds, diseases, pests and pollution [6].

The WOFOST model was developed as part of studies on food safety and potential world food production conducted by the Centre for World Food Studies (CWFS) in cooperation with the Wageningen Agricultural University. WOFOST belongs to the group of models developed in Wageningen by De Wit school, which also comprises such models as SUCROS, ARID CROP, MARCOS or ORYZA [7, 8]. There is a group of several models of plant growth and development considering the impact of diseases and weeds on the amount of production (eg DSSAT or INTERCOM).

In field conditions radiation and temperature are the basic factors determining the amount of potential production of cultivated crops. *Photosynthetically active radiation* (PAR) – wavelength $\lambda = 400–700$ nm is useful for plants. Other radiation ranges have diversified influence on the course of physiological processes in plants (Table 1). For computations of potential production it is most frequently assumed that PAR constitutes half of total radiation which reaches the canopy.

Table 1

The radiation effect upon plants [9]

Wave length	Effect on plants
< 280	Fast plant death
280–315	Harmful for most plants
315–400	Shortening of plants, leaf thickening
400–510	Large absorption by chlorophyll and xantophylls
510–610	Low photosynthetic activity
610–720	Strong absorption by chlorophyll
720–1000	Lengthening of plants
> 1000	No specific physiological effect

Explanatory (mechanistic) models are based on determining canopy gross photosynthesis depending on photosythetically active radiation reaching the canopy, temperature, water availability, leaf area, carbon dioxide concentration, photosynthetic output of single leaves and many stressors. The number of assimilates produced (gross photosynthesis) is diminished by the value of maintenance and growth respiration. These models work according to daily or even shorter time-step. This type of computations is included in many models developed at the Wageningen Agricultural University (Fig. 1).

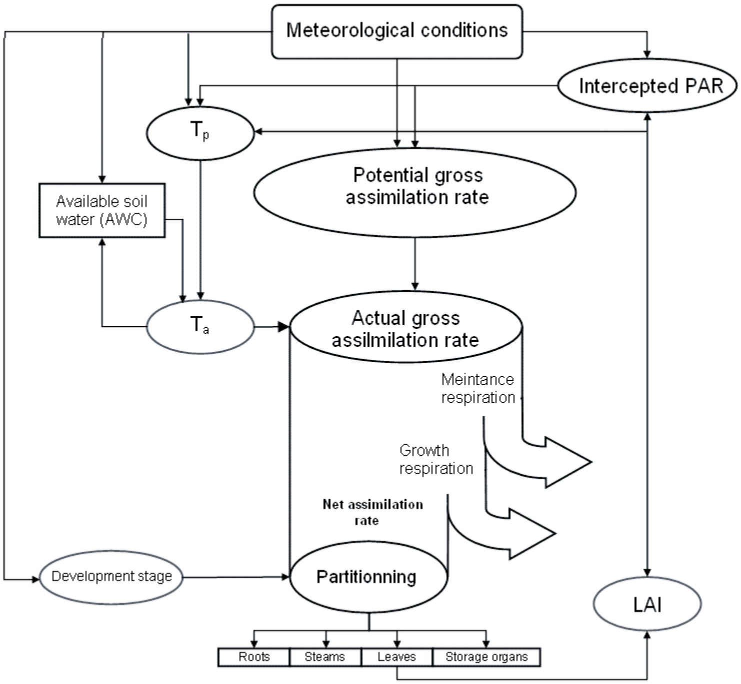

Fig. 1. The general diagram of the WOFOST model (Ta, Tp – actual and potential transpiration rate), Boogaard et al [10] modified

In another approach the estimation of biomass production is based on the coefficient of *light use efficiency* (LUE) or radiation use efficiency (RUE). The amount of radiation reaching the canopy is converted directly into the amount of produced carbohydrates using a conversion coefficient. This method has been applied in many models, such as CropSyst, DSSAT, APSIM, LINTUL and others [4].

Simulation of plant development in deterministic models is conducted with daily or longer time-step. Plant development in the models is determined by the increment of the effective temperature sum and the length of day, whereas in some models it is based also on the vernalization process. The temperature influences not only the speed of plant development but also the intensity of photosynthesis, evapotranspiration and respiration, which has been described by appropriate equations [4, 10–12].

In many plant growth and development models (including WOFOST), production limited by water deficit is computed through multiplication of potential output by actual to potential transpiration (evapotranspiration) ratio. It may be assumed with great probability that *potential assimilation* (Ap) and *actual assimilation* (Ar), *potential yield* (Qp) and *actual yield* (Qr) correspond to *potential* (ETp) and *actual evapotranspiration* (ETa). This statement may assume the following form:

$$\frac{Q_r}{Q_p} = \frac{A_r}{A_p} = \frac{ET_a}{ET_p}$$

Passioura [13] introduced a formula to compute the usable yield (Y) in conditions limited by water deficit:

$$Y = WUE \cdot T \cdot HI$$

where: WUE – coefficient of water utilization (g d.m./kg H_2O),
T – transpiration (g H_2O/g d.m. $\cdot$ m^2),
HI – harvest index.

The majority of plant growth and development models calculate the production limited by nutrient (most often nitrogen) availability and in a limited number also the other microelements. Moreover, some models consider also the effect of aluminium ions, connected with soil environment acidification and soil salinity on the amount of production (Table 2). These issues were discussed in detail in the papers by de Baros [14], Kulig [4] and others. The Daisy model has a "pesticides" module which considers pesticide dispersion in the environment: uptake by leaves, volatilization, absorption by the root system, pesticide decomposition in the soil environment or leaching [15].

Table 2

Comparison of selected plant growth and development models considering yield determinants [14]

Name of model	Weather	Soil water	Nutrient availability	Toxic substances
SUCROS	+	+	—	—
CENTURY	+	+	N, P, S	—
WOFOST	+	+	N, P, K	—
CANDY	+	+	N	—
Daisy	+	+	N	—
N-SIM	+	+	N	—
EPIC	+	+	N, P	Al, salinity
CROPGRO	+	+	N	—
EPICSEAR	+	+	N, P, K	Al, Na

The DSSAT packet (including CERES model family) belongs to a small group of models simulating, beside quantitative, also qualitative features of yield, eg protein concentrations in cereal grains. The amount of protein accumulated in grain depends, among others, on the temperature, water and nitrogen deficit stress [16].

Conclusion

Modeling plant growth and development is a specific synthesis of interdisciplinary knowledge in the field of yield physiology, agroclimatology, agronomy and soil science. Therefore it provides plenty of useful information for proper interpretation and better understanding of the researched process. Knowledge gained in this way may be used for conducting the so-called simulation experiment using models, which may be of crucial importance for research on the agricultural environment protection (eg pesticide, biogens or heavy metal migration and transformation in soil).

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CZYNNIKI ABIOTYCZNE W MODELACH ROŚLINNYCH

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Abstrakt: W ostatnim ćwierćwieczu XX w. nastąpił dynamiczny rozwój modeli opisujących wzrost, rozwój i plonowanie roślin. Szczególną grupę stanowią modele wyjaśniające (mechanistyczne) mechanizmy zjawiska (ang. *explanatory model*). Modelowanie akumulacji biomasy przedstawiane jest najczęściej na trzech poziomach produkcyjności: potencjalnej, limitowanej dostępnością wody i składników pokarmowych oraz osiągalnej (redukowanej przez obecność chwastów, chorób i szkodników). Modelowanie dostarcza wielu cennych informacji służących właściwej interpretacji i lepszemu zrozumieniu badanego procesu. Uzyskana w ten sposób wiedza może służyć do przeprowadzania za pomocą modeli tzw. eksperymentów symulacyjnych, co może mieć szczególne znaczenie w badaniach związanych z ochroną środowiska rolniczego (np. przemieszczanie się i przemiany pestycydów, biogenów lub metali ciężkich w glebie).

Słowa kluczowe: matematyczne modele roślin, czynniki abiotyczne

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Ryszard MAZUREK[1] and Anna PIOTROWSKA[2]

INFLUENCE OF BLACK LOCUST (*Robinia pseudoacacia* L.) SHELTERBELTS ON THE CONTENT AND FRACTIONAL COMPOSITION OF HUMUS IN ARABLE SOIL DEVELOPED FROM LOESS

WPŁYW ZADRZEWIEŃ ROBINII AKACJOWEJ (*Robinia pseudoacacia* L.) NA ZAWARTOŚĆ I SKŁAD FRAKCYJNY PRÓCHNICY GLEBY UPRAWNEJ WYTWORZONEJ Z LESSU

Abstract: The objective of the study was to evaluate the influence of black locust afforestation adjacent to arable loess soil on its fractional humus composition. Fractional humus composition was assessed according to Boratynski and Wilk. The content of total humus and humus fractions decreased with the distance from black locust afforestation. It was observed the dependance of distance from trees on decrease of humus fractions strictly connected with mineral phase (IV fraction) and humines. Therefore their higher concentrations in the zones adjacent to the trees was an evidence of a beneficial role of black locust on soil organic matter composition. Amount of movable humus fractions content (I fraction) was lower in the field zones close to the trees (15.3 %) than in those 12 m from the afforestation (19.1 %). Average values of the ratio HAC/FAC was a bit higher in the zone 0–12 m away from the trees (1.03) in comparison with the more distant ones (0.91).

Key words: *Robinia pseudoacacia*, black locust, humus

Black locust (*Robinia pseudoacacia* L.) due to its small edaphic requirements is used for planting on all types of wasteland, primarily in dry and poor soils [1]. Robinia plantings are frequently used for reclamation of former opencast mines and in the areas destroyed by improper human activity [2].

On agricultural lands of the Proszowice Plateau and Miechow Upland black locust shelterbelts are quite frequent, the trees were planted there among others to reinforce the loess ravines and at the same time for high quality wood fuel [3].

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Robinia lives in a symbiosis with *Baciullus radicola* nodule bacteria and bacteria of *Rhizobium* species. Therefore, its influence on increasing nitrogen content in soils is a commonly known fact [4–6]. On the other hand there is no literature data concerning the effect of black locust shelterbelts on the quantity and quality of humus in ploughlands [7].

The research aimed to determine the effect of black locust shelterbelts adjoining a ploughland on fractional composition of humus in arable soil developed from loess.

Material and methods

Soil samples were collected from the 0–20 cm layer of a microplot situated in Krolewice village at the Proszowice Plateau, marked out on an arable field adjoining black locust shelterbelts. The trees forming the shelterbelts are between 20 and 30 years old. The shelterbelts are formed exclusively from robinia trees, the undergrowth is poor, mainly composed of herbaceous plants counted by some to *Chelidonio-Robinietum* alliance, which is associated with allelopatic effect of robinia trees on the other plant species [8].

The 20 m × 24 m microplot was divided into 12 zones (2 m wide) at growing distance from the trees and 5 microplots with area of 2 m × 4 m were sepaarted in each zone. Samples representing each zone were taken from the microplots. In 60 samples collected in this way organic carbon content was assessed using Tiurin method in Oleksynowa modification and converted into organic substance content. In collective samples representing each zone, humus fractional composition was determined using Boratynski and Wilk method. The results of humus content assessments were elaborated geostatistically using Surfer 8.0 Programme. The data were subjected to statistical analysis using post-hoc Tukey test in Statistica 7.0 programme.

Results and discussion

The soil cover of the analyzed field consists of brown soils (*Eutric Cambisol*) developed from loess. The analyzed brown soil which represented the soil cover of the researched area was characterized by clay silt granulation. Acid reaction (pH = 4.72) was assessed in the humus horizon. The highest contents of total nitrogen and organic carbon were registered in the arable-humus horizon Ap (respectively 0.17 % and 1.40 %).

The highest content of humus (over 2.80 %) was determined in the soil samples taken at the distance of 12 m from the robinia shelterbelts (Fig. 1, Table 1). The exception was the 2–4 m zone, where 2.75 % humus was assessed. Humus content was diminishing visibly with the distance from the shelterbelts and in the farthest zone (22–24 m) did not exceed 2.45 %. On the basis of Tukey test statistically significant differences in humus contents at the significance level 0.05 were registered between the 0–8 m and 8–24 m zones.

It evidences a humus forming role of black locust in the first place affecting the arable field zones close to the shelterbelts. These values confirm previous results of

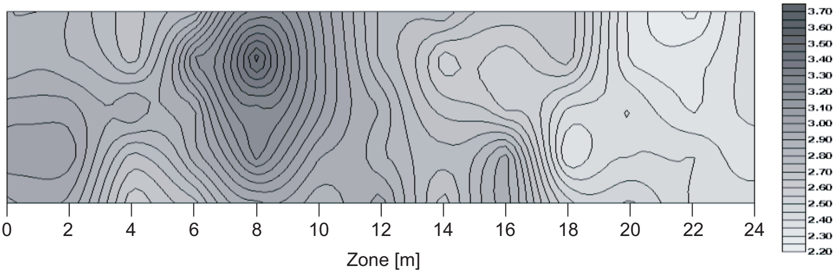

Fig. 1. Humus content [%] in particular zones

research conducted in China stating the identical role of robinia, particularly on sandy soils [9]. The influence of shelterbelts on humus content in soil was apparent in the zones situated up to 10 m from the trees, which is a distance comparable with their height.

Table 1

Significance level of differences (calculated on the base of the Tukey test) between average humus content in soils of particular zones (differences are significant if $p < 0.05$)

Zone [m]	0–2	2–4	4–6	6–8	8–10	10–12	12–14	14–16	16–18	18–20	20–22	22–24
Average humus content, %	2.93	2.75	2.92	3.23	3.00	2.86	2.70	2.73	2.54	2.43	2.36	2.42
0–2		0.57	1.00	0.02	1.00	1.00	0.18	0.42	< 0.01	< 0.01	< 0.01	< 0.01
2–4	0.57		0.66	< 0.01	0.11	0.97	1.00	1.00	0.32	0.01	< 0.01	< 0.01
4–6	1.00	0.66		0.02	0.99	1.00	0.24	0.51	< 0.01	< 0.01	< 0.01	< 0.01
6–8	0.02	< 0.01	0.02		0.23	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
8–10	1.00	0.11	0.99	0.23		0.82	0.02	0.06	< 0.01	< 0.01	< 0.01	< 0.01
10–12	1.00	0.97	1.00	< 0.01	0.82		0.67	0.91	0.01	< 0.01	< 0.01	< 0.01
12–14	0.18	1.00	0.24	< 0.01	0.02	0.67		1.00	0.76	0.07	< 0.01	0.05
14–16	0.42	1.00	0.51	< 0.01	0.06	0.91	1.00		0.45	0.02	< 0.01	0.02
16–18	< 0.01	0.32	< 0.01	< 0.01	< 0.01	0.01	0.76	0.45		0.95	0.51	0.93
18–20	< 0.01	0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.07	0.02	0.95		1.00	1.00
20–22	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.51	1.00		1.00
22–24	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.05	0.02	0.93	1.00	1.00	

The contents of isolated humus compounds was declining with the distance from the shelterbelts: from 1.62 % C (0–2 m zone) to 1.02 % C (22–24 m zone) (Fig. 2). A negative effect of the distance from false acacia on the content of humus substances most strongly bound to mineral soil fraction (humines) was found, as well as humus substances separated in IV extraction (using $0.1\ \mathrm{mol \cdot dm^{-3}}$ NaOH solution) determined as strongly bound to mineral soil phase [10]. Higher contents of these fractions in the

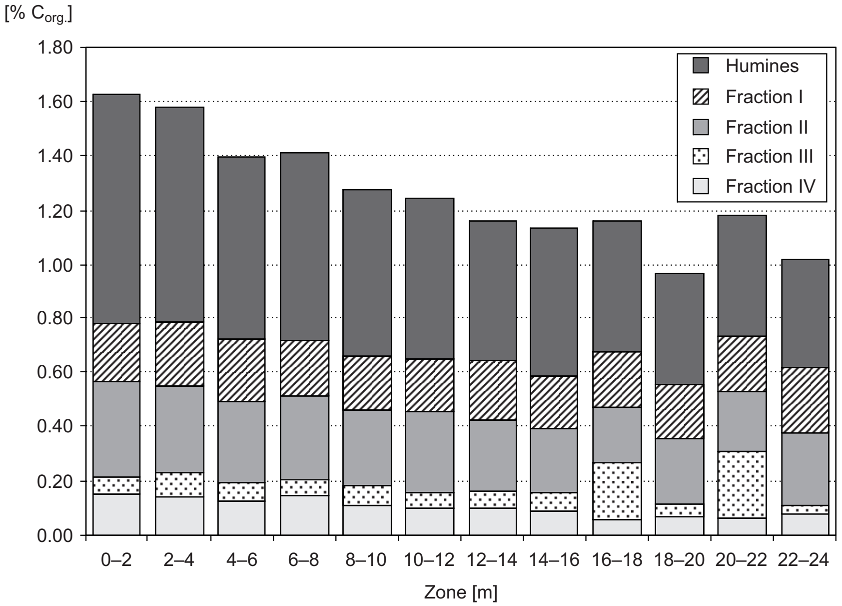

Fig. 2. Humus compounds extracted in particular extractions [% of $C_{org.}$]

zones adjoining the trees testifies a positive effect of acacia on humus composition. Percentage of mobile humus bonds (fraction I) was lower in the zones up to 12 m from the acacia (on average 15.3 %) in comparison with the 12–24 m zones (on average 19.1 %).

Table 2

HAC/FAC ratio of humus compounds in particular extractions

Zone [m]	Extraction I	Extraction II	Extraction IV	Total
0–2	0.82	1.20	1.35	1.09
2–4	0.77	1.14	1.96	1.11
4–6	0.41	1.18	1.42	0.86
6–8	0.85	1.15	1.24	1.06
8–10	0.70	1.24	1.21	1.01
10–12	0.89	0.99	1.72	1.05
12–14	0.54	1.04	1.10	0.82
14–16	0.64	1.14	1.12	0.92
16–18	0.68	1.20	1.06	0.92
18–20	0.59	1.03	1.23	0.85
20–22	0.73	1.65	0.91	1.09
22–24	0.58	1.03	1.16	0.83

The greatest amounts of leaves, branches and pods fall in the area of the microplot closest to the shelterbelts. Fallen black locust leaves revealing a low C:N ratio are fast decomposed and provide an additional source of nitrogen in the soils [11]. Nitrogen originating from organic mater decomposition and from the process of atmospheric N assimilation by root bacteria may be easily transformed into humus substances with highest process of humification [7]. It was corroborated by the obtained mean value of humic to fulvic acids ratio (Table 2). HAC/FAC ratio computed for the zones distanced up to 12 m from the shelterbelts was higher that the one calculated for the zones > 12 m far from the trees (respectively 1.03 and 0.91).

Conclusions

1. The highest content of humus was assessed in the soil samples collected at the distance of 12 m from black locust trees.
2. A negative effect of the distance from the acacia on the humin and humus substances content strictly connected with soil mineral phase was determined.
3. A percentage of mobile humus bonds was lower in the zones 0–12 m far from black locust in comparison with 12–24 m zones.
4. HAC/FAC ratio computed for the zones distanced up to 12 m from the shelterbelts was higher than calculated for the zones > 12 m far from the trees.

Acknowledgement

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WPŁYW ZADRZEWIEŃ ROBINII AKACJOWEJ (*Robinia pseudoacacia* L.) NA ZAWARTOŚĆ I SKŁAD FRAKCYJNY PRÓCHNICY GLEBY UPRAWNEJ WYTWORZONEJ Z LESSU

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Abstrakt: Celem badań było określenie wpływu zadrzewień robinii akacjowej sąsiadujących z użytkiem ornym na skład frakcyjny próchnicy lessowej gleby uprawnej. Skład frakcyjny próchnicy określono, stosując metodę Boratyńskiego i Wilka. Zawartość próchnicy i wydzielonych połączeń próchnicznych malała wraz z odległością od zadrzewień. Stwierdzono ujemny wpływ odległości od robinii na zawartość humin oraz substancji próchnicznych ściśle związanych z mineralną fazą gleby (frakcja IV). Wyższa zawartość tych frakcji w strefach sąsiadujących z drzewami jest dowodem korzystnego oddziaływania robinii na skład próchnicy. Średnia wartość stosunku CKH/CKF obliczona dla stref oddalonych do 12 m od zadrzewień była większa niż obliczona dla stref bardziej oddalonych od drzew (odpowiednio 1,03 i 0,91).

Słowa kluczowe: *Robinia pseudoacacia*, grochodrzew, próchnica

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Grzegorz MIKICIUK[1] and Małgorzata MIKICIUK[2]

INFLUENCE OF THREE TYPES OF SOIL AND MINERAL FERTILIZATION ON THE CONTENT OF ASSIMILATION PIGMENTS IN THE LEAVES OF CELERY (*Apium graveolens* L. var. *rapaceum* (Mill.) Gaud.)

WPŁYW TRZECH TYPÓW GLEB I ZRÓŻNICOWANEGO NAWOŻENIA MINERALNEGO NA ZAWARTOŚĆ BARWNIKÓW ASYMILACYJNYCH W LIŚCIACH SELERA KORZENIOWEGO (*Apium graveolens* L. var. *rapaceum* (Mill.) Gaud.)

Abstract: In a town of Doluje near Szczecin, at the Experimental Station of the Market Gardening Chair, University of Agriculture in Szczecin, a two-factor vegetation experiment (microfield) in the system of complete randomization was carried out in three replications. It was a two year experiment. The first experimental factor was the type of soil: proper black earth, muck soil and proper pseudogley soil. The second factor was the level of NPK fertilization (0 – 0, 0, 0 kg $\cdot$ ha^{-1}; I – 75, 33, 100 kg $\cdot$ ha^{-1}; II – 150, 66, 200 kg $\cdot$ ha^{-1}). Celery, var. *rapaceum* (Mill) Gaud., cultivar Diamant was the biological material for the studies. At five dates of the harvesting, the content of assimilation pigments (chlorophyll *a*, chlorophyll *b*, total chlorophyll and carotenoids), in the celery leaves was determined. A significant effect of both experimental factors on the concentration of chlorophyll as well as on carotenoids in the leaves of the examined plant was observed.

Keywords: *Apium graveolens* L. var. *rapaceum*, NPK fertilization, assimilation pigments, proper black earth, muckous soil, proper pseudogley soil

One of the ways of adaptation of a plant to environment is a change in the composition of its tissues. According to Chroboczek and Skapski [1] such compounds as vitamins, proteins, carbohydrates, organic acids, oils, phytoncides and mineral salts determine the biological value of vegetables. A physiological feature of plants that contains information about, among other things, the state of their supply with some

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macro- and microelements such as: nitrogen. magnesium, iron, manganese, copper or zinc, is the content of assimilation pigments in photosynthetic organs of the indicator plant. In the conducted studies, celery (*Apium graveolens* L. var. *rapaceum* (Mill.) Gaud.) was selected to be an indicator plant. Celery is a very popular vegetable plant, a rich source of mineral salts of potassium, sodium, calcium, magnesium, phosphorus and iron, and also vitamins, particulary vitaminum C [2]. This plant needs a lot of nitrogen, phosphorous and potassium. It is also characterized by quite large soil demands. It the case of celery it is essential to apply optium mineral fertilization for the soil conditions in which it is grown.

The studies were aimed to assess the content of assimilation pigments in the leaves of the indicator plant cultivated on three types of soil of different physicochemical properties, at differentiated mineral fertilizing with NPK.

Material and methods

A two-factor vegetation experiment (microplot) in the system of complete randomization was carried out in three replications in Doluje near Szczecin, at the Experimental Station of the Market Gardening Chair, University of Agriculture in Szczecin. It was a two year experiment. The first experimental factor was the type of soil: typical black earth (A), muck soil (B) and typical pseudogley soil (C). The main features differentiating the soils were as follows: the mechanical composition, the sorptive properties, pH value, and the content of macro- and microelements (Table 1) [3]. In each year of the studies experiments were carried out on three types of soil on three research sites.

Table 1

Physico-chemical properties of soils

Soil	Genetic horizon	Depth [cm]	Percent of clay fraction [%]	pH		C-organic	N-total	P-available	K-available
				H_2O	KCl	[%]		[mg · 100 g^{-1}]	
A*	A1p	0–10	16	6.7	6.1	1.17	0.11	11.79	15.89
	A2p	10–20	15	7.0	6.4	0.91	0.11	11.62	16.68
	Aa	20–60	15	7.1	6.5	0.61	0.07	2.64	12.49
B	A(M)1	0–10	16	7.6	6.9	1.80	0.20	23.32	16.71
	A(M)2	10–20	15	7.7	7.0	1.88	0.20	22.88	20.98
	A(M)3	20–40	15	7.7	7.1	1.78	0.27	17.16	15.58
C	A1p	0–10	32	7.7	6.8	1.18	0.13	10.56	15.08
	A2p	10–20	32	7.8	7.0	0.94	0.13	12.67	12.29
	A3h	20–40	39	6.9	6.3	0.84	0.10	3.60	7.59

* A – proper black earth, B – muck soil, C – proper pseudogley soil.

The second factor was the level of NPK fertilization (0 – 0, 0, 0 kg · ha^{-1}; I – 75, 33, 100 kg · ha^{-1}; II – 150, 66, 200 kg · ha^{-1}). Nitrogen, phosphorus and potassium fertilization was applied in the forms of ammonium nitrate, triple superphosphate and potassium sulphate. Fertilization was performed on 15 May, before planting the seedlings on the experimental plots. The area of one microplot was 3 m^2. Celery, var. *rapaceum*, cultivar Diamant was the biological material for the studies. The seedlings of this plant taken from the Assessment of Potato Cultivars Station in Szczecin were planted with a spacing of 30 × 30 cm.

Using Lichtenthaler and Wellburn's method [4], at five dates of harvesting (4 and 29 July, 23 August, 15 September, 18 October), the content of assimilation pigments in the leaves in three replications was determined. The content of chlorophyll *a*, *b*, total and carotenoids was computed following Arnon et al [5]. The data in the tables show averages of the five dates of harvesting.

The results and discussion

Assimilation pigments play a role of photoreceptors in the process of CO_2 assimilation in plants. Thus, their content is a reflection of photosynthetic activity. In higher plants, two kinds of chlorophyll, ie *a* and *b*, take part in the process of photosynthesis. The ratio of chlorophyll *a* to *b* in plants of the moderate climate varies from 2.3 to 5.5 [6, 7].

In the first year of the studies the significantly smallest amount of chlorophyll was characteristic of the leaves of celery non-fertilized with NPK (level 0). A significant difference was also recorded between the content of this dye in the leaves of celery cultivated in typical black earth and in a muck soil, whereas in the second year of the studies no significant influence of experimental factors on the amount of chlorophyll *a* in the leaves of the indicator plant was observed (Table 2).

The content of chlorophyll *b* in the leaves of celery in both years of the studies depended significantly on the level of NPK fertilization, the type of soil and the interaction of these factors, for the significantly smallest concentration of this dye was noticed in plants growing in a muck soil, non-fertilized with NPK. It amounted, in the first and in the second year, to 0.303 and 0.290 $mg \cdot g^{-1}$ fm, respectively (Table 2).

In both years of the studies, the level of mineral fertilization had, a significant impact on the content of total chlorophyll in the leaves of *Apium graveolens*. In the first year, the smallest content of this photosynthetic pigment was observed in plants non-fertilized with NPK (1.161 $mg \cdot g^{-1}$ fm), in the second year a significant difference was recorded between the concentration of total chlorophyll in the leaves of plants from the combination of non-fertilized and fertilized plants at level II (Table 2)

Carotenoids are pigments which, according to Devlin and Baker [8], protect chlorophyll from photooxidation, convey light energy to chlorophyll and partly participate in the assimilation of CO_2. Non significant effect of soil type on the content of these pigments in the leaves of the indicator plant was observed. However in both years a significantly larger concentration of carotenoids in the leaves of plants fertilized with the largest doses of NPK (level II) than in the leaves of non-fertilized plants (level 0) was recorded.

Table 2

Content of chlorophyll *a*, *b*, *a*+*b* and carotenoids in leaves of *Apium graveolens* [mg · g^{-1} f.m.]

Soil	I year				II year			
	Level of fertilization			Mean II	Level of fertilization			Mean II
	0	I	II		0	I	II	
Chlorophyll *a*								
A	0.879 ab*	1.118 b	0.962 ab	0.986 b	0.844 a	0.888 a	0.937 a	0.890 a
B	0.611 a	0.859 ab	0.921 ab	0.797 a	0.623 a	0.864 a	0.928 a	0.805 a
C	0.782 ab	0.866 ab	0.947 ab	0.865 ab	0.854 a	0.871 a	0.774 a	0.833 a
Mean I	0.757 a	0.948 b	0.943 b		0.774 a	0.874 a	0.880 a	
Chlorophyll *b*								
A	0.447 b	0.466 b	0.505 b	0.473 b	0.427 a	0.446 a	0.486 a	0.453 b
B	0.303 a	0.441 b	0.479 b	0.408 a	0.290 b	0.421 a	0.485 a	0.399 a
C	0.459 b	0.457 b	0.462 b	0.459 b	0.466 a	0.432 a	0.433 a	0.444 b
Mean I	0.403 a	0.455 b	0.482 b		0.394 a	0.433 ab	0.468 b	
Chlorophyll *a*+*b*								
A	1.327 ab	1.585 b	1.467 b	1.460 b	1.271 ab	1.334 b	1.423 b	1.343 a
B	0.914 a	1.300 ab	1.400 ab	1.205 a	0.913 a	1.285 ab	1.413 b	1.204 a
C	1.241 ab	1.323 ab	1.408 b	1.324 ab	1.320 b	1.302 b	1.207 ab	1.277 a
Mean I	1.161 a	1.402 b	1.425 b		1.168 a	1.307 ab	1.348 b	
Carotenoids								
A	0.475 ab	0.506 ab	0.527 b	0.503 a	0.459 ab	0.504 b	0.532 b	0.499 a
B	0.366 a	0.470 ab	0.500 ab	0.445 a	0.357 a	0.477 ab	0.518 b	0.451 a
C	0.444 ab	0.442 ab	0.490 ab	0.459 a	0.436 ab	0.449 ab	0.495 ab	0.460 a
Mean I	0.428 a	0.473 ab	0.506 b		0.417 a	0.477 ab	0.515 b	

* Averages denoted with the same letters do not differ significantly at the level of significance α = 0.05.

Increasing fertilization with NPK caused, independently of the type of soil, an increase in the amount of both chlorophyll and carotenoids in the celery leaves. A particularly significant positive impact of the largest dose of fertilizer was observed. Similar results were recorded by Podsiadlo et al [9] and by Smolik and Malinowska [10]. They showed a stimulating effect of mineral NPK fertilization on the content of chlorophyll *a* and *b* and carotenoids in the leaves of legumes and spring wheat.

Conclusions

1. Increasing doses of NPK resulted in an increase in the content of chlorophyll in the leaves of celery var. *rapaceum* cultivated in all types of soil.
2. The smallest amount of assimilation pigments was characteristic of the leaves of the indicator plant, non-fertilized with NPK.
3. The least favourable properties in respect of the influence on the content of chlorophyll in the photosynthetic organs of celery was characteristic of a muck soil.

4. Diverse physicochemical properties of soils did not affect the content of carotenoids in the assimilation organs of celery.

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WPŁYW TRZECH TYPÓW GLEB I ZRÓŻNICOWANEGO NAWOŻENIA MINERALNEGO NA ZAWARTOŚĆ BARWNIKÓW ASYMILACYJNYCH W LIŚCIACH SELERA KORZENIOWEGO (*Apium graveolens* L. var. *rapaceum* (Mill.) Gaud.)

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Abstract: W Stacji Doświadczalnej Katedry Warzywnictwa Akademii Rolniczej w Szczecinie, w miejscowości Dołuje koło Szczecina przeprowadzono dwuletnie, dwuczynnikowe doświadczenie wegetacyjne (mikropoletkowe), w układzie kompletnej randomizacji, w trzech powtórzeniach. Pierwszy czynnik doświadczalny stanowił typ gleby: czarna ziemia właściwa, gleba murszowa i gleba opadowo-glejowa właściwa. Drugim czynnikiem był poziom nawożenia NPK (0 – 0, 0, 0 kg · ha^{-1}; I – 75, 33, 100 kg · ha^{-1}; II – 150, 66, 200 kg · ha^{-1}). Biologiczny materiał badań stanowił seler korzeniowy, odmiana Diamant. W pięciu terminach zbioru oznaczono zawartość w liściach selera barwników asymilacyjnych (chlorofilu *a*, chlorofilu *b*, całkowitego oraz karotenoidów). Stwierdzono statystycznie istotny wpływ obu czynników doświadczalnych na koncentrację zarówno chlorofilu, jak i karotenoidów w liściach badanej rośliny.

Słowa kluczowe: *Apium graveolens* L. var. *rapaceum*, nawożenie NPK, barwniki asymilacyjne, czarna ziemia właściwa, gleba murszowa, gleba opadowo-glejowa właściwa

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OPTIMIZATION OF LAWN FERTILIZATION WITH NITROGEN. PART III. DYNAMICS OF SOIL MICROBIOLOGICAL COMPOSITION AND ENZYMATIC ACTIVITY OF DEHYDROGENASES

OPTYMALIZACJA NAWOŻENIA AZOTOWEGO TRAWNIKA CZ. III. DYNAMIKA SKŁADU MIKROBIOLOGICZNEGO GLEBY. AKTYWNOŚĆ ENZYMATYCZNA DEHYDROGENAZ

Abstract: The aim of this study was to determine the effect of increasing nitrogen fertilization of lawns (at doses corresponding to 0, 50, 100, 150 and 200 mg N dm^{-3} soil) on dynamics of changes in microbial community composition of soil: total counts of fungi, bacteria, *Actinomycetes*, oligotrophic and copiotrophic bacteria, as well as enzymatic activity of dehydrogenases. No significant effect was found of analyzed levels of nitrogen fertilization on counts of microorganisms and enzymatic activity of soil. A trend, although not confirmed statistically, could be observed for microbial counts to increase in case of the N 150 combination. A factor significantly modifying the microbial community composition and enzymatic activity of soil was sampling date and related atmospheric conditions. A significant increase of total bacterial counts was recorded at the 2nd sampling date (in April). The quantity of *Actinomycetes* increased towards the end of the summer period (August), while the highest enzymatic activity of dehydrogenases was determined in July. The contents of copiotrophs and oligotrophs in soil decreased significantly with the duration of vegetation.

Keywords: nitrogen fertilization, dehydrogenases activity, fungi, bacteria, oligotrophic and copiotrophic bacteria

Cultivation, fertilization, protection and contamination of soil modify its physico-chemical properties as well as change its biological activity. A measure of biological activity, comprising all occurring compound and energy conversions, may be enzymatic activity [1] and dynamics of development of selected groups of microorganisms living in the soil. It depends both on the type of soil, the depth of the soil profile, vegetation

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cover, atmospheric conditions as well as cultivation regime and fertilization of soil, and many other factors affecting soil [2–6].

Factors having an effect on the activity of microorganisms in soil, their quality and quantity, include eg contents of organic substances, nitrogen compounds, macro- and microelements, water, oxygen as well as pH and temperature of soil.

The level as well as the manner of soil inhabitation by microorganisms depends to a considerable degree on contents of such readily available nutrients in soil, such as sugars, proteins and fats. The occurrence of microorganisms is also determined by the presence of allopathic substances in the soil, which are secreted by plant roots, as well as interactions between different groups of microorganisms [7]. The population size of soil microorganisms is considerably influenced by fertilization, including organic and mineral nitrogen fertilization, applied in order to supply plants with nutrients [8].

The aim of the conducted investigations was to determine the effect of increasing lawn fertilization with nitrogen on the dynamics of changes in the microbial community composition of soil (total counts of bacteria, fungi, *Actinomycetes*, oligotrophic and copiotrophic) as well as microbiological activity expressed as dehydrogenases activity.

Material and methods

Vegetation experiments were conducted in the years 2007–2008 at the ‘Marcelin’ Experimental Station of Departments of the Faculty of Horticulture, the Poznan University of Life Sciences. Analyses were conducted on five increasing nitrogen lawn fertilization levels (in mg N dm^{-3}) of 0, 50, 100, 150, 200 (denoted as N 0, N 50, N 100, N 150 and N 200). The control was combination N 0, in which no fertilization with nitrogen was applied. Contents of phosphorus, potassium and magnesium in all tested combinations were supplemented to standard levels (in mg dm^{-3}): P 100, K 200, Mg 180 (2007) and 300 (2008). Soil samples for microbiological analyses were collected at the following dates: 15.03, 15.04, 12.06, 08.07 and 19.08.2008. Each time from a given combination a total of 14–18 individual samples were collected from the topsoil (0–20 cm), from which a representative mixed sample (0.4–0.5 dm^3) was produced after mixing. Air temperature at a height of 5 cm above the ground was recorded using a HOBO Weather Station by ONSET. The course of its changes is presented in Fig. 1.

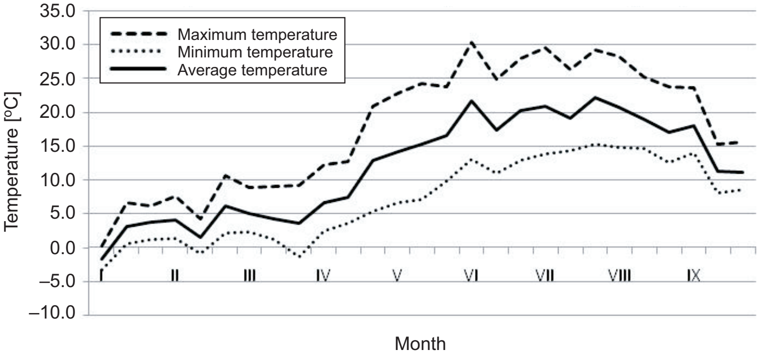

Fig. 1. Dynamics of changes in air temperature at a height of 5 cm above the ground

Microbiological analyses

In soil samples collected from the radical zone counts of microorganisms were determined using the plate method on respective agar media (in five replications). The mean number of colonies was calculated as converted to 1 g^{-1} d.m. of soil:

– The total bacterial counts were determined on a medium from a soil extract after 14-day incubation at 25 ^{o}C;

– Fungi were determined on Martin's medium after 5-day incubation at 24 ^{o}C [9];

– *Actinomycetes* were determined on a medium according to Pochon after 5-day culture at 25 ^{o}C [10];

– Copiotrophs were determined on the NB medium after 5-day incubation at 25 ^{o}C [11];

– Oligotrophs were determined on the DN medium after 5-day incubation at 25 ^{o}C [12].

Enzymatic analyses

The analysis of enzymatic activity of soil fertilized with varied doses of nitrogen was based on the determination of dehydrogenases activity using colorimetry, with 1 % TTC (*triphenyltetrazole chloride*) applied as a substrate, after 24-h incubation at 30 ^{o}C, at a wavelength of $\lambda = 485$ nm and it was expressed in [$cm^3 \cdot H_2 \cdot kg^{-1} \cdot 24\ h^{-1}$].

Dynamics of changes in microbial community composition of soil and enzymatic activity of dehydrogenases were analyzed statistically using the Duncan test. Inference was performed at significance level $\alpha = 0.05$.

Results and discussion

In the conducted experiment a differentiating effect of nitrogen fertilization was found – among other things – on the dynamics of microbiological changes in soil. A trend, although not confirmed statistically, could be observed for the counts of microorganisms in soil to increase with an increase in the intensity of fertilization. Earlier studies showed a similar trend, concerning total bacterial count (eg from genera *Arthrobacter*, *Bacillus* and *Pseudomonas*), total count of fungi (eg from genera *Fusarium* and *Penicilium*) and *Actinomycetes* (from genus *Streptomycetes* sp.) [13]. Several studies confirmed a significant differentiating effect of fertilization, particularly with nitrogen, on counts of soil microorganisms as well as their species composition [14–16].

In the analyses conducted by the authors of this study no differentiating effect was found for either nitrogen fertilization or vegetation period on the total population of fungi in soil (Table 1). A trend could be observed, although it could not be proved statistically, for the amounts of this group of microorganisms to increase in case of the combination intensively fertilized with nitrogen (N 150, N 200). Soil fungi, mainly moulds, are capable of nitrogen uptake not only from organic compounds, but also ammonium and nitrate salts. The highest levels of these microorganisms among tested combinations were determined in July at a fertilization level of 150 kg N (56.0

CFU × 10^5). Recorded pH values of soil in this combination were minimally lower than in the other combinations, which could have promoted the development of this group of microorganisms.

Table 1

The effect of varied nitrogen fertilization on fungal count (CFU × 10^5 g^{-1} d.m. of soil)

N level	Month					
	March	April	June	July	August	Mean
N 0	36.0	20.0	20.0	13.0	6.0	19.0a
N 50	23.0	30.0	23.0	33.0	20.0	25.8a
N 100	20.0	5.0	20.0	30.0	30.0	21.0a
N 150	30.0	31.0	12.0	56.0	20.0	29.8a
N 200	36.0	10.0	26.0	20.0	40.0	26.4a
Mean	29.0a	19.2a	20.2a	30.4a	23.2a	

The level of analyzed fungi in soil did not undergo significant periodical changes. However, their biggest mean number was recorded at the 1st sampling date (in March) and at the 4th sampling date (in July), amounting to 29.0 and 30.4 CFU × 10^5, respectively. At the other dates of analyses their level was markedly lower. In turn, at the onset of flowering (2nd date) in the control combination (with no nitrogen fertilization) the lowest count of fungi was determined, which could have resulted from an increased soil moisture content and slightly higher pH.

Similarly as in case of fungi, no significant effect was found of tested nitrogen fertilization levels on total bacterial count in soil (Table 2). It ranged from 48.3 (N 50) to 86.5 CFU × 10^6 (N 150). Vegetation period was the factor significantly modifying the count of this group of microorganisms. A significant increase in bacterial content in soil was found in April (113.4 CFU × 10^6), which could have been connected with atmospheric conditions and an increase with mean soil temperature over 5 °C (Fig. 1), causing an increase in microbiological activity. The highest total bacterial count among all the tested combinations was recorded in April at fertilization N 150 (223.0 CFU × 10^6). Lower bacterial counts in June, July and August could have been caused by an increased level of fungi and *Actinomycetes*. Earlier studies confirmed the varied dynamics of microbiological changes during vegetation [17]. Those authors indicated that the highest microbiological activity of soil is observed usually in spring.

Table 2

The effect of varied nitrogen fertilization on total bacterial count (CFU × 10^6 g^{-1} d.m. of soil)

N level	Term					
	March	April	June	July	August	Mean
N 0	63.3	92.3	46.0	12.3	38.3	50.4a
N 50	21.3	77.2	76.3	37.3	29.3	48.3a
N 100	43.6	61.3	71.6	42.0	34.0	50.5a
N 150	63.6	223.0	24.3	56.3	65.3	86.5a
N 200	71.3	113.0	24.0	39.0	41.3	57.7a
Mean	52.6b	113.4a	48.4b	37.4b	41.6b	

No differentiating effect of nitrogen fertilization on the count of *Actinomycetes* in soil was shown in this study. Vegetation period was a factor significantly modifying the count of this group of microorganisms (Table 3), similarly as in case of the above-mentioned groups of microorganisms. Their mean count was stable and ranged from 17.5 (N 200) to 23.7 CFU × 10^6 (N 50). However, their highest number was recorded in summer months in case of combination N-150 (51.4 CFU × 10^6).

Table 3

The effect of varied nitrogen fertilization on *Actinomycetes* count (CFU × 10^6 g^{-1} d.m. of soil)

N level	Month					
	March	April	June	July	August	Mean
N 0	9.7	11.1	19.4	13.1	41.6	19.0a
N 50	7.7	14.1	20.2	42.7	33.9	23.7a
N 100	8.3	10.3	16.9	29.9	27.5	18.6a
N 150	9.9	11.0	14.0	31.6	51.4	23.6a
N 200	12.2	12.1	12.9	21.1	29.3	17.5a
Mean	9.6b	11.7b	16.7b	27.7a	36.7a	

In fertile soils the level of *Actinomycetes* is usually lower than that of bacteria (the ratio of bacteria and *Actinomycetes* counts is then 60 : 40). In most analyzed samples the determined content of bacteria was higher than that of *Actinomycetes*, except for the 4th and 5th dates in combinations N 0 and N 50, where the population of *Actinomycetes* dominated over bacteria, which could have resulted from the too low nitrogen content in soil.

Another group of microorganisms, which counts were determined in the course of this experiment, comprised oligotrophic bacteria. They are microorganisms, which grow well in a medium with an exceptionally low level of available organic compounds. Optimal concentration of nutrients for oligotrophic bacteria ranges from 1 to 15 mg dissolved C dm^{-3}. The term oligotrophy refers to bacteria, which grow on a poor medium, with a low nutrient concentration only at the onset of culture [18]. They are bacteria exhibiting low variability in terms of their population size and activity. These organisms are highly sensitive to amino acids, organic acids, vitamins and inorganic salts, such as NaCl and KCl [19].

In the conducted experiment the amount of oligotrophic bacteria in soil underwent significant periodical changes within a year. It was highest at the beginning of the spring period (in March), and next it decreased significantly (Table 4).

Considerable amounts of root exudates of grasses, which could have contained amino acids, carbohydrates, vitamins, organic acids, enzymes and metal ions most probably could have inhibited the growth and development of analyzed oligotrophic bacteria.

An upward trend could be observed, although not proved statistically, for the count of oligotrophic in soil to increase in case of combinations intensively fertilized with nitrogen. Their mean content ranged from 78.9 (N 0) to 128.9 CFU × 10^6 (N 150).

Table 4

The effect of varied nitrogen fertilization on oligotrophic bacteri count (CFU × 10^6 g^{-1} d.m. of soil)

N level	Month					
	March	April	June	July	August	Mean
N 0	232.0	63.0	32.0	11.0	56.6	78.9a
N 50	118.0	172.0	83.6	52.3	68.0	98.8a
N 100	195.0	119.0	86.3	85.3	103.3	117.8a
N 150	203.0	170.0	47.6	103.3	120.6	128.9a
N 200	229.0	129.0	25.0	69.6	132.0	116.9a
Mean	195.4a	130.6b	54.9c	64.3c	96.1c	

What is more, no significant effect was found of nitrogen fertilization on total count of copiotrophic bacteria in soil (Table 5). Their content ranged from 36.5 (N 100) to 59.6 CFU × 10^6 (N 150). Similarly as in case of oligotrophic bacteria, the content of copiotrophic bacteria was highest in the spring period (March, April) and next it was significantly reduced with the time of vegetation. It is a specific group of soil microorganisms proliferating intensively during the influx of organic matter to soil, mainly in the form of fresh plant and animal residue. Their nutrient requirements are thus connected with high concentrations of organic components in the substrate, which optimal dose is approx. 1000 mg dissolved C dm^{-3} [20]. The population size of oligotrophic bacteria decreases relatively fast after the readily available nutrient substrate is depleted, as a result of autolysis of most cells or the other cells entering the latent phase.

Table 5

The effect of varied nitrogen fertilization on copiotrophic bacteria count (CFU × 10^6 g^{-1} d.m. of soil)

N level	Month					
	March	April	June	July	August	Mean
N 0	94.0	101.3	15.3	6.0	27.6	48.8a
N 50	63.4	78.0	30.0	7.6	25.0	40.8a
N 100	77.6	42.6	22.3	10.6	29.3	36.5a
N 150	73.0	184.6	7.0	15.3	18.0	59.6a
N 200	95.3	61.3	6.6	17.3	31.6	42.4a
Mean	80.7a	93.6a	16.2b	11.4b	26.3b	

Assuming that metabolic activity of microorganisms is manifested in the activity of their enzymes, changes in the activity of dehydrogenases in soil were considered in the experiment. Their level of activity determines the rate of redox changes in the soil medium, which characterizes a given soil, being a measure of its fertility [21]. No significant effect was observed in the conducted analyses of nitrogen fertilization on enzymatic activity of dehydrogenases in soil, which was similar in all tested combinations (Table 6). However, a significant increase in enzymatic activity of dehydrogenases was recorded in the summer (in July). In the opinion of Sinsabaugh et al [22], activity of enzymes is connected not only with a given plant species or plant development phase, but it also depends on the amount of plant residue, the depth of root systems and temperature. Pawluczuk [23] also confirmed a significant effect of changes in soil temperatures on occurring enzymatic processes. In turn, Amdor et al [24] stressed a strong relationship between activity of enzymes and soil properties (pH, organic carbon content, etc.).

Table 6

The effect of varied nitrogen fertilization on enzymatic activity of dehydrogenases

N level	Month					
	March	April	June	July	August	Mean
N 0	0.013	0.004	0.004	0.017	0.003	0.008a
N 50	0.004	0.003	0.004	0.021	0.006	0.008a
N 100	0.012	0.003	0.007	0.099	0.005	0.025a
N 150	0.008	0.008	0.009	0.021	0.007	0.011a
N 200	0.008	0.005	0.013	0.060	0.009	0.019a
Mean	0.009b	0.005b	0.007b	0.043a	0.006b	

Regular microbiological changes in soil, apart from the quantitative composition of the microbial community composition, are also shown by the interrelations between their individual groups. The following microbiological indexes are considered:

A the quantitative ratio of bacteria to *Actinomycetes*;

B the ratio of total count of bacteria to that of fungi;

C the quantitative ratio of oligotrophic to copiotrophic bacteria.

In fertile soils bacteria predominate in terms of their number over *Actinomycetes* (ratio **A** = 60 : 40). In most analyzed combinations the determined count of bacteria was higher than that of *Actinomycetes* (apart from the 4th and 5th date in combinations N 0 and N 50). Based on the above, it may be stated that soil in case of combinations intensively fertilized with nitrogen was characterized by good fertility. An increased number of *Actinomycetes* over bacteria in the above-mentioned combinations could be explained by a reduced amount of nutrients as well as inferior water and air relations. In poor soils higher contents of *Actinomycetes* may be found, since soil quality is one of the factors having a selective effect on them.

In the opinion of some researchers [25, 26] another microbiological index of soil fertility (**B**), based on the ratio of fungi to the total bacterial count, expresses more accurately biological properties of soil than the count of each of these groups separately. Moreover, it indicates compensatory dependencies in the development of communities of bacteria and fungi, also observed by other authors (Weyman-Kaczmarek and Pedziwilk) [27]. Dominance of fungi over bacteria shows a higher ability of fungi, than that of bacteria, to survive under deteriorating environmental conditions. Such an undesirable phenomenon was not recorded in the discussed experiment.

Another significant index of microbiological activity of soil is also the ratio of oligotrophic to copiotrophic bacteria (**C**). It is an index of biological balance, indicating an appropriate direction of microbiological changes of soil organic matter. In the conducted experiment in all combinations the proportion of oligotrophic bacteria predominated in the soil microflora. The above dominance is appropriate and necessary for the maintenance of a constant level of organic matter.

Mineral nitrogen is utilized by many bacteria and fungi in their metabolism. By uptake of ammonium and nitrate ions they affect the acidity of the external medium. More readily available ammonium salts contribute to the acidification of the substrate, while nitrates cause its alkalization. Organic nitrogen is most readily available in the form of amino acids, which are used as a source of nitrogen and energy material. Certain microorganisms absorbing nitrogen require only those amino acids, which they are not capable of synthesizing (this concerns mainly auxotrophic microorganisms).

Conclusions

1. No differentiating effect was found of fertilization with nitrogen on total counts of fungi, bacteria, *Actinomycetes,* copiotrophic and oligotrophic bacteria in soil as well as the enzymatic activity of dehydrogenases. A trend for the microbial count to increase could be observed, although not proved statistically, in case of combination N 150.
2. A factor significantly modifying the levels of microorganisms and dehydrogenases activity in soil was sampling date and related atmospheric conditions.
3. A significant increase of the total bacterial count in soil was determined in spring (April), while that of *Actinomycetes* – towards the end of the summer period (August). The highest enzymatic activity of dehydrogenases was recorded for soil in July. With the duration of vegetation the contents of copiotrophic and oligotrophic bacteria in soil decreased.

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OPTYMALIZACJA NAWOŻENIA AZOTOWEGO TRAWNIKA. CZ. III. DYNAMIKA SKŁADU MIKROBIOLOGICZNEGO GLEBY. AKTYWNOŚĆ ENZYMATYCZNA DEHYDROGENAZ

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Abstrakt: Celem przeprowadzonych badań było określenie wpływu wzrastającego nawożenia azotowego pod trawnikiem (w dawkach odpowiadających: 0, 50, 100, 150 i 200 mg N dm^{-3} gleby) na dynamikę zmian składu mikrobiologicznego gleby: ogólnej liczby grzybów, bakterii, promieniowców, oligotrofów i kopiotrofów, a także aktywność enzymatyczną dehydrogenaz. Nie stwierdzono znaczącego wpływu badanych poziomów nawożenia azotowego na liczebność mikroorganizmów i aktywność enzymatyczną gleby. Zarysowała się, nie udowodniona statystycznie, tendencja do wzrostu liczebności mikroorganizmów w przypadku kombinacji N 150. Czynnikiem istotnie modyfikującym skład mikrobiologiczny i aktywność enzymatyczną gleby był termin pobierania próbek i związane z nim warunki atmosferyczne. Znaczny wzrost ogólnej liczby bakterii stwierdzono w II terminie pobierania próbek (w kwietniu). Liczba promieniowców znacznie wzrastała pod koniec okresu letniego (sierpień), a największą aktywność enzymatyczną dehydrogenaz oznaczono w lipcu. Wraz z trwaniem wegetacji wyraźnie obniżała się zawartość kopiotrofów i oligotrofów w glebie.

Słowa kluczowe: żywienie azotem, aktywność dehydrogenaz, grzyby, bakterie, oligotrofy i kopiotrofy

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EFFECT OF FOLIAR FERTILIZATION WITH TYTANIT ON THE DRY MATTER YIELD AND MACROELEMENTS' CONTENT IN THE MEADOW SWARD

WPŁYW NAWOŻENIA DOLISTNEGO TYTANITU NA PLON SUCHEJ MASY I ZAWARTOŚĆ MAKROELEMENTÓW RUNI ŁĄKOWEJ

Abstract: One-factor field experiment was designed by the method of random blocks sampling in four replications (fields of the 2.0 × 5.0 m area). The experimental field was characterized with the brown, acidic soil, classified to the V quality class. The field experiment was conducted in the years 2006–2008, in the private, individual farm in the administrative district of Pilica, within Zawiercie County, at the region of Krakow-Czestochowa Jura, located on the altitude of 320 m.

The spraying with the Tytanit fertilizer in three different concentrations: 0.02, 0.04 and 0.08 % constituted an experimental factor. Tytanit applied in a concentration of 0.04 % affected on average 52 % higher dry matter yield when compared with the control object. Moreover, foliar application of Tytanit in the concentration of 0.04 % resulted in the highest growth of the content of all examined macroelements. The difference in relation to the control object amounted to 28 % for phosphorus, 78 % for potassium, 80 % for calcium, 81 % for magnesium and 60 % for sodium. Higher dosage of the preparation (0.08 %) decreased the concentration of the investigated macroelements when compared with the 0.04 % variant and in some cases even with the 0.02 % variant.

Keywords: meadow sward, titanium, yield, macroelements

Recently more and more attention has been paid to ensure the proper fertilization to the plants, which cover their requirements for the fundamental components like: nitrogen, phosphorus and potassium as well as suitable amounts of microelements. Although the latter elements are assimilated only in small amounts they are required for the proper proceeding of many biochemical and physiological processes in plants.

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Titanium is one of the very important microelements which positively affects the biochemical processes proceeding in plants leading to the speeding and enhancement of the plant yielding [1–3]. Titanium fertilization stimulates the activity of many enzymes, eg: catalase, peroxidase, lipooxigenase or nitrate reductase. Moreover, it influences the speeding of metabolic processes, promotes pollination, fertilization as well as setting of fruits and seeds. Titanium affects the increase of chlorophyll concentration in leaves, promotes their growth and development. Titanium not only accelerates the plant growth and development but also decreases plant sensitivity to the unfavourable environmental conditions, increases resistance to fungal and bacterial diseases. Fertilization with titanium positively affects the assimilation of other components from the soil and other fertilizers [4]. The investigations on the effect of titanium on the increase of plant yield have been conducted mainly on the vegetables and agricultural plants and the results of these experiments confirm the positive effect of this fertilization. On the other hand, there is a little number of scientific papers concerning the effect of titanium fertilization on the meadow flora yielding. Majority of the foliar microelement fertilizers contain the minimal titanium concentrations.

Thus the aim of three-year field experiment was an estimation of the effect of Tytanit foliar fertilization on the dry matter yield and the content of macroelements in the meadow sward.

Materials and methods

The field experiment was conducted in the years 2006–2008 in the private farm in Solca, in the Pilica administrative district. It was established by means of random block sampling with four replications on the brown, acidic soil (pH_{KCL} = 5.2) of a V quality class. The soil contained medium level of assimilable potassium, manganese and zinc and was poor in assimilable phosphorus and copper.

During the vegetation period (April–September) the average rainfall amounted to 338.1; 375.4 and 320.3 mm, respectively in the year 2006, 2007 and 2008, whereas average air temperatures reached the values of 15.2; 14.3 and 14.9 ^{o}C, respectively.

The experiment included four objects: the control (without using the preparation) and three variants sprayed with Tytanit in three different concentrations: 0.02, 0.04 and 0.08 %. The preparation was used once for each regrowth. The first spraying was applied at the beginning of the spring vegetation, the next one after the harvesting at the stage of initial sward regrowth but not later than 3 weeks before the next mowing. During the research the fundamental mineral fertilization was also applied which comprised: 80 kg N $\cdot$ ha^{-1} for the first regrowth, 60 kg N $\cdot$ ha^{-1} for the second and third regrowths in the form of ammonium saltpetre. The phosphorus was utilized once in the spring, in the amount of 120 kg $P_2O_5 \cdot$ ha^{-1} as a triple superphosphate and potassium for the first and third regrowths in a dose of 60 kg $K_2O \cdot$ ha^{-1} for each regrowth as a 57 % potassium salt. The area of each field amounted to 10 m^2.

The collected plant material was subjected to the analysis of the forage chemical composition, the dry matter content by drying at 105 ^{o}C, phosphorus and magnesium content by the colorimetric vanadium-molybdenic method, potassium, sodium and calcium by the flame photometric method [5].

The results were subjected to the analysis of variance and verified using Tukey test at the significance level of $\alpha = 0.05$.

Results and discussion

The conducted study revealed that foliar application of Tytanit preparation in different concentrations (0.02 %, 0.04 % and 0.08 %) significantly affected the dry matter yield of the meadow sward. In all examined fertilization variants these treatment had a positive yielding effect. The plants treated with foliar fertilizer provided greater dry matter yield than the plants from the control object. The lowest average yields of dry matter for three years were collected with the sward of the control object (Table 1). The sward fertilized with Tytanit in a concentration of 0.02 % increased the yield by 2.47 $\mathrm{Mg \cdot ha^{-1}}$. The following values of the yield were observed for the sward fertilized with Tytanit in a concentration of 0.08 and 0.04 %. The latter treatment resulted in the average 14.42 $\mathrm{Mg \cdot ha^{-1}}$ dry matter yield which was higher from the respective value noticed for the control object by 52 %. The sward of the examined objects gave the highest yield in the year 2007 and the lowest level was found in 2008. The difference between the results of dry matter yield observed for these years amounted to 15.5 % for the fertilized objects and 11.1 % for the control and was statistically significant. The positive effect of foliar application of the selected fertilizers on the plant yielding was reported by Faber et al [6], Czuba et al [7], Szewczuk [8], Kocon and Grenda [3] and others. According to Faber et al [6] the beneficial effect of foliar fertilization on the plant condition results from the activation of its metabolism what leads to the higher assimilation of the nutrients by the root systems. Moreover, these results are consistent with the findings of many authors [3, 4, 6, 9–11], who proved that foliar fertilization of wheat, rape and other plants positively affected photosynthesis and efficiency of the nitrogen utilization and in a consequence influenced higher yield of the plants.

Table 1

The dry matter yields of the meadow sward

Tytanit concentration	Years			Means for the years (2006–2008)	
	2006	2007	2008		
	$[\mathrm{Mg \cdot ha^{-1}}]$				[%]
Control	9.74	9.81	8.83	9.46	100
0.02 %	12.02	12.24	11.54	11.93	126
0.04 %	13.98	15.82	13.45	14.42	152
0.08 %	13.43	14.52	11.84	13.26	140
$\mathrm{LSD}_{0.05}$	1.38	2.23	1.67	—	—

Applied foliar fertilization with Tytanit the highest impact had on a calcium content in the meadow flora (Table 2). The highest level of this element was determined for the

Table 2

The effect of different Tytanit concentrations on the macroelements' content in the meadow sward

Tytanit concentration	Content of macroelements [$g \cdot kg^{-1}$ d.m.]														
	P			K			Ca			Mg			Na		
	2006	2007	2008	2006	2007	2008	2006	2007	2008	2006	2007	2008	2006	2007	2008
Control	2.83	2.06	3.11	15.10	14.61	15.61	4.28	2.91	8.53	0.98	0.82	1.18	0.16	0.09	0.19
0.02 %	3.00	2.16	3.90	23.97	18.16	31.52	5.35	4.79	13.20	1.27	1.50	1.52	0.16	0.14	0.24
0.04 %	3.03	2.94	4.25	26.27	21.89	32.51	7.69	6.78	13.91	1.61	1.82	1.93	0.22	0.17	0.30
0.08 %	2.87	2.28	3.62	24.30	21.47	26.76	6.79	5.12	13.20	1.53	1.34	1.58	0.18	0.14	0.28
Mean	2.93	2.36	3.72	22.41	19.03	26.60	6.03	4.90	12.21	1.35	1.37	1.55	0.18	0.14	0.25
$LSD_{0.05}$	ns	0.49	0.45	3.28	2.43	5.02	1.41	1.60	1.45	0.22	0.38	0.32	ns	ns	0.04

plants from the object sprayed with the Tytanit preparation in a concentration of 0.04 %. The plants collected from this object contained 92 % higher sodium concentration than plants from the control object (mean contents for three years). As a result of foliar treatment with 0.02 and 0.08 % Tytanit preparation a significant growth of mean calcium content when compared with the control object was also found – the difference reached the level of 48 and 63 %, respectively. High diversity as affected by the foliar application of titanium was found for magnesium content. The most significant increase of this component was observed after the application of 0.04 and 0.08 % concentration. The difference in relation to the control object was equal to 84 and 52 %, respectively.

Our investigations revealed also that foliar application of titanium also affected potassium and sodium contents. As an effect 66 % and 46 % higher mean levels of respectively potassium and sodium were noticed as a result of titanium utilization. Tytanit applied in a concentration of 0.04 % increased potassium and sodium contents, whereas higher dose (0.08 %) slightly decreased the level of these elements. The least diversified were results obtained for the phosphorus content – 17 % in relation to the control object. The highest values were noticed after the treatment with Tytanit in a concentration of 0.04 % and the lowest (without the control object taking into consideration) for the object sprayed with 0.08 % concentration. Marcinek and Hetman [12] also reported the increment of macroelements' content in plants as a result of Tytanit fertilization.

The obtained positive effect on yielding as well as higher concentration of the examined macroelements under the treatment with titanium indicates that the foliar fertilization of the meadow sward with this component is recommended even if the cultivation conditions suggest that availability of the nutrients is good.

Conclusions

1. The utilization of Tytanit fertilizer in three different concentrations significantly affected dry matter yield of the meadow sward. Tytanit applied in a concentration of 0.04 % increased the dry matter yield by 52 % in relation to the control object.

2. Tytanit application significantly influenced the calcium content in the meadow flora. Foliar treatment with titanium in a concentration of 0.04 % and 0.08 % resulted in significantly increased mean content of this element in comparison with the non-fertilized object. The difference reached the value of 92 and 63 %, respectively.

3. The fertilization with titanium lead to 66, 61 and 46 % higher mean content of potassium, magnesium and sodium, respectively.

4. The highest growth of the content of examined macroelements was found in the object fertilized with Tytanit in a concentration of 0.04 %. This variant resulted in 70 % (on average) higher content of all macroelements in relation to the control object.

5. Higher concentration of the preparation (0.08 %) decreased the content of examined macroelements in comparison with the 0.04 % concentration, and in some cases also in relation to the concentration of 0.02 %.

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WPŁYW NAWOŻENIA DOLISTNEGO TYTANITU NA PLON SUCHEJ MASY I ZAWARTOŚĆ MAKROELEMENTÓW RUNI ŁĄKOWEJ

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Abstrakt: Jednoczynnikowe doświadczenie polowe założono metodą losowanych bloków, w czterech powtórzeniach (poletka o wymiarach 2,0 × 5,0 m). Na polu doświadczalnym występowała gleba brunatna kwaśna, zaliczana pod względem bonitacyjnym do klasy V. Doświadczenie prowadzono w latach 2006–2008, w indywidualnym gospodarstwie rolnym położonym w gminie Pilica, powiat zawierciański na Jurze Krakowsko-Częstochowskiej, na wysokości powyżej 320 m n.p.m.

Czynnikiem doświadczenia był oprysk nawozem Tytanit w trzech stężeniach: 0,02, 0,04 i 0,08 %. Tytanit stosowany w stężeniu 0,04 % zwiększył plon suchej masy w stosunku do obiektu kontrolnego średnio o 52 %.

Ponadto stwierdzono, iż dolistne zastosowanie Tytanitu w stężeniu 0,04 % spowodowało największy wzrost zawartości wszystkich badanych makroelementów. Różnica ta w porównaniu z obiektem kontrolnym wynosiła dla fosforu 28 %, dla potasu 78 %, dla wapnia 80 %, dla magnezu 81 % i dla sodu 60 %. Większe stężenie preparatu (0,08 %) zmniejszyło zawartość badanych makroelementów w porównaniu do preparatu o stężeniu 0,04, a w niektórych przypadkach nawet do oprysku o stężeniu 0,02 %.

Słowa kluczowe: ruń łąkowa, tytan, plon, makroelementy

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QUALITY OF THE GRASS-LEGUME SWARD AS AFFECTED BY THE PHOSPHORUS-POTASSIUM FOLIAR FERTILIZATION

JAKOŚĆ RUNI TRAWIASTO-MOTYLKOWATEJ NA TLE DOLISTNEGO NAWOŻENIA FOSFOROWO-POTASOWEGO

Abstract: The investigations were conducted in the years 2006–2008 on the grass-legume sward, on the brown acidic soil classified to the V quality class. The aim of the experiment was to evaluate the influence of the foliar fertilization with Alkalin PK 10:20 (phosphorus and potassium fertilizer) on the yielding and the quality of the meadow sward.

Foliar application of the Alkalin increased the dry matter yield by the 11 % (on average) in relation to the control object. Moreover, it was found that foliar utilization of Alkalin resulted in the increased organic components' content (total protein, raw fat) and the concentration of mineral components (raw ash, phosphorus, potassium, calcium and sodium). The application of this preparation in a dose of 3.0 $dm^3 \cdot ha^{-1}$ caused the average growth of the above-mentioned components by 14, 33, 32, 38, 44, 58 and 42 %, respectively, when compared with the control object. On the other hand, decreased contents of the crude fiber as well as its ADL and NDF fraction were observed.

Keywords: meadow sward, foliar fertilization, yield, quality

Many investigations proved that plants assimilate nutrients not only through the root system, but also by the aboveground parts. The plants can even 80–10-time more efficiently assimilate components by the leaf surface than by the roots. Foliar fertilization has many advantages, first of all gives the possibility of fast and effective supplementation of the deficiency of nutrients directly to the leaves, regardless of the water availability in the soil as well as root system functioning [1, 2]. Therefore, the foliar fertilization is especially important when the root system is not fully developed as well as during dry periods [3].

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The response of plants on the applied foliar fertilization depends first of all on the plant species, the form of fertilizer, concentration and frequency of its application as well as at which stage of plant growth it is utilized. This fertilization is beneficial not only for the yielding but also for the plant resistance to diseases, pests and droughts [4].

Moreover, because of the lower concentration of the active substance foliar fertilization constitutes lower environmental load in comparison with the soil fertilizers. The investigations revealed that during the first year after the application only approximately 10–12 % of phosphorus is utilized, the remaining amount is accumulated in the soil or washed out [5].

Because of the plant high susceptibility to the leaf damage the foliar fertilization requires precise control of the amount of dosage and the term of its application.

Despite many conducted examinations there is no unequivocal estimation of the effect of the foliar fertilization with macroelements on the level and quality of the yield, therefore the aim of the three-year field study was to evaluate the influence of the foliar fertilization with phosphorus and potassium on the quality of the grass-legume sward.

Materials and methods

The field experiment was conducted in the years 2006–2008 in the individual farms located in the administrative district of Gmina Pilica. The investigation was established by the method of random block sampling, in four replications, on the brown, acidic soil ($pH_{KCl} = 5.2$), of the V quality class. The soil contained medium level of assimilable potassium, manganese and zinc and was poor in assimilable phosphorus and copper.

During the vegetation period (April–September) the average rainfall amounted to 338.1; 375.4 and 320.3 mm, respectively in the year 2006, 2007 and 2008, whereas average air temperatures reached the values of 15.2; 14.3 and 14.9 ^{o}C, respectively.

The experiment included four objects: the control (without using the preparation) and three variants sprayed with Alkalin PK 10:20 (150 g P_2O_5, 300 g K_2O in 1 dm^3 of fertilizer). The preparation was used once for each regrowth in three different doses: 1.5 $dm^3 \cdot ha^{-1}$, 2.0 $dm^3 \cdot ha^{-1}$ and 3.0 $dm^3 \cdot ha^{-1}$. The first spraying was applied at the beginning of the spring vegetation, the next one after the harvesting at the stage of initial sward regrowth but not later than 3 weeks before the next mowing. During the research the fundamental mineral fertilization was also applied which comprised: 80 kg $N \cdot ha^{-1}$ for the first regrowth, 60 kg $N \cdot ha^{-1}$ for the second and third regrowths in the form of ammonium saltpetre. The phosphorus was utilized once in the spring, in the amount of 120 kg $P_2O_5 \cdot ha^{-1}$ as a triple superphosphate and potassium for the first and third regrowths in a dose of 60 kg $K_2O \cdot ha^{-1}$ for each regrowth as a 57 % potassium salt. The area of each field amounted to 10 m^2.

The collected plant material was subjected to the analysis of the fundamental organic components' content by the Weenden's method, phosphorus and magnesium content by the colorimetric vanadium-molybdenic method, potassium, sodium and calcium by the flame photometric method [6, 7].

The results were subjected to the analysis of variance and verified using Tukey test at the significance level of $\alpha = 0.05$.

Results and discussion

Our investigations revealed that foliar application of Alkalin PK in different doses (concentrations of 1.5 $dm^3 \cdot ha^{-1}$, 2.0 $dm^3 \cdot ha^{-1}$ and 3.0 $dm^3 \cdot ha^{-1}$) significantly affected the dry matter yield of the meadow flora. In all fertilization variants it had a positive yielding effect. Plants supplemented with the foliar preparation yielded higher amounts of dry matter when compared with the control object. The mean yield for three years of the investigations was the lowest in the case of the control sward (Table 1). The yield determined for the sward fertilized with Alkalin in a dose of 1.5 $dm^3 \cdot ha^{-1}$ was higher by 0.52 $Mg \cdot ha^{-1}$ followed by the variants fertilized with the concentration of 2.0 $dm^3 \cdot ha^{-1}$ and 3.0 $dm^3 \cdot ha^{-1}$ of this fertilizer. The latter resulted in 10.87 $Mg \cdot ha^{-1}$ average dry matter yield and it was higher in relation to the control variant by 15 %. The highest dry matter yield was observed for the examined swards in the year 2007, the lowest in 2008. The mean difference amounted to 8 % – for the fertilized objects and 8.7 % – for the control object and was statistically significant. The foliar fertilization is one of the factor of the modern production technology affecting the yield level and its quality. Conventional soil fertilization not always ensures the availability of the components required for the achievement of the high level and high quality yield [2, 8–9].

Table 1

The dry matter yields of the meadow sward

Dose of fertilizer	Years			Mean for the years (2006–2008)	
	2006	2007	2008		
	[$Mg \cdot ha^{-1}$]				[%]
Control	9.74	9.81	8.83	9.46	100
Alkalin 1	9.98	10.43	9.54	9.98	106
Alkalin 2	10.54	10.73	10.12	10.46	111
Alkalin 3	10.87	11.32	10.42	10.87	115
$LSD_{0.05}$	0.44	0.56	0.52	0.51	—

Alkalin 1 – dose of 1.0 $dm^3 \cdot ha^{-1}$; Alkalin 2 – dose of 2.0 $dm^3 \cdot ha^{-1}$; Alkalin 3 – dose of 3.0 $dm^3 \cdot ha^{-1}$.

Under the foliar fertilization the assimilation of the nutrients is much faster than the assimilation by the root system [5]. Already during the 4–5 hours after the treatment 80 % of the fertilizer is assimilated by the plant. It is assumed that utilization of the mineral components from the foliar fertilizer reaches 90 %. Foliar fertilizers are characterized with the complete solubility in water and do not penetrate into the underground water. Foliar fertilization can also contribute to the increase of the yield even by the several dozen percent [5, 9–12].

Utilized foliar fertilization with Alkalin had the greatest influence, among all organic components, on the content of ADL fraction (17.38 %), total protein (14.76 %) and raw fat (12.20 %) of the meadow flora (Table 2). The highest diversifications in the content of selected mineral components was found in the concentrations of calcium (23.35 %), phosphorus (16.42 %), potassium (16.24 %). The highest levels of these elements were determined for the object where Alkalin in a dose of 3.0 $dm^3 \cdot ha^{-1}$ was applied.

Table 2

The content of nutrients in the meadow sward

Content [$g \cdot kg^{-1}$ d.m.]	Object				$LSD_{0.05}$
	Control	Alkalin 1	Alkalin 2	Alkalin 3	
Raw ash	68.1	68.9	71.2	77.3	3.24
Total protein	80.6	81.5	82.3	107.4	7.27
Crude fiber	283.5	279.0	281.0	281.2	2.15
Raw fat	23.5	29.9	30.3	31.1	5.15
Non-nitrogen extract	544.3	540.7	535.2	503.0	27.51
ADF	323.1	326.8	329.1	329.4	3.96
ADL	37.6	27.1	27.3	27.3	2.70
NDF	543.8	531.8	535.6	536.0	4.95
P	2.34	2.38	2.45	3.24	0.26
K	16.31	23.16	23.22	23.53	5.19
Ca	3.51	3.64	3.72	5.53	0.58
Mg	1.03	1.04	1.04	1.06	ns
Na	0.12	0.14	0.15	0.17	0.02

Explanations as in Table 1.

Under the conditions of the high level of phosphorus and potassium deficiency foliar interventional fertilization with these elements is highly recommended. Phosphorus is the most easily assimilated in the form of phosphoric acid (H_3PO_4). It is transported slowly through the plant but faster than in the case it is assimilated through the root system. Foliar supplementation with phosphorus accelerates the plant growing, increases yielding and affects decreased level of mechanical breakages [2]. Application of potassium increases the efficiency of photosynthesis and respiration as well as decreases the losses caused by diseases [12].

Diversified phosphorus and potassium fertilization caused significant increment of the dry matter yield and the content of the examined components. The best results were achieved under the high level of fertilization (3.0 $dm^3 \cdot ha^{-1}$), which were significantly higher than the values observed for the lowest (1.5 $dm^3 \cdot ha^{-1}$), and also medium (2.0 $dm^3 \cdot ha^{-1}$) level of fertilization.

Conclusions

1. The utilization of Alkalin fertilizer in three different doses positively affected the dry matter yield of the meadow sward. Alkalin applied in a dose of 3.0 $dm^3 \cdot ha^{-1}$ increased the dry matter yield by 15 % when compared to the control object.

2. Application of Alkalin had a significant influence on the total protein and raw fat content in the meadow flora. Foliar treatment with this preparation in a dose of 3.0 $\mathrm{dm}^3 \cdot \mathrm{ha}^{-1}$ caused the significant growth of the concentration of these components, which were respectively 33 and 32 % higher than the value found for the non-fertilized object.

3. The phosphorus-potassium fertilization in the amount of 3.0 $\mathrm{dm}^3 \cdot \mathrm{ha}^{-1}$ resulted in the increased phosphorus, potassium, calcium and sodium content, by respectively 38, 44, 58 and 42 % when compared with the control object.

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JAKOŚĆ RUNI TRAWIASTO-MOTYLKOWATEJ NA TLE DOLISTNEGO NAWOŻENIA FOSFOROWO-POTASOWEGO

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Abstrakt: Badania przeprowadzono w latach 2006–2008 na runi trawiasto-motylkowatej, na glebie brunatnej kwaśnej, zaliczanej pod względem bonitacyjnym do klasy V. Celem eksperymentu było określenie wpływu nawożenia dolistnego Alkalinu PK 10:20 (nawóz fosforowo-potasowy) na plonowanie oraz jakość runi łąkowej.

Dolistna aplikacja Alkalinu zwiększyła plon suchej masy w stosunku do obiektu kontrolnego średnio o 11 %. Ponadto stwierdzono, iż dolistne zastosowanie Alkalinu spowodowało wzrost zawartości składników organicznych: białko ogólne, tłuszcz surowy oraz składniki mineralne: popiół surowy, fosfor, potas, wapń i sód. Zastosowanie tego nawozu w dawce 3,0 $dm^3 \cdot ha^{-1}$ powodowało wzrost zawartości wymienionych składników odpowiednio o 14, 33, 32, 38, 44, 58 i 42 % w porównaniu z obiektem kontrolnym.

Natomiast odnotowano zmniejszenie zawartości dla włókna surowego oraz frakcji ADL i NDF.

Słowa kluczowe: ruń łąkowa, nawożenie dolistne, plon, jakość

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EFFECT OF SHADING WITH VARIOUS COLOURED FILMS ON THE YIELD AND QUALITY OF CELERY AND BUTTERHEAD LETTUCE

WPŁYW CIENIOWANIA FOLIĄ O RÓŻNYM ZABARWIENIU NA PLON I JAKOŚĆ SELERÓW NACIOWYCH ORAZ SAŁATY MASŁOWEJ

Abstract: In 2005–2007 at the University of Agriculture in Krakow field experiments with shading with polyethylene films were carried out on medium-early celery ‘Tango’ cultivar and butterhead lettuce ‘Melodion’ cultivar.

Shadings with transparent, white and black films made from original and recycled materials were fixed on low tunnel structures on 7 days before harvesting lettuce (from 23.05.2005. and 23.05.2006, respectively) and on 10–12 days before harvesting celery (from 29.06.2005, 1.07.2006 and 25.06.2007, respectively). The best elongation growth of celery was shown under white film which also slightly increased the yield of celery stalks. In relation to yielding of celery in 2005 best effect was obtained under white film, in the next year under transparent and white film and in the last year of the experiment the yield was even in all objects with small advantage under white film. Shading lettuce with transparent film for 7 days before harvest increased the yield and soluble sugars content in plants. With the decrease of PAR permeability through films dry matter, soluble sugars and ascorbic acid content decreased in celery and lettuce. No differences were shown in the growth, quality and yield of celery and lettuce grown under films made from original and recycled materials.

Keywords: butterhead lettuce, celery, shading, polyethylene films, yield, quality

The use of shadings in vegetable production is connected with limitation of light that reaches plants. Films and non-wovens in various colours or double layers of these materials used as covers in low tunnels structures decrease permeability for PAR (*Photosynthetically Active Radiation*) by 10–70 %. Different radiation and thermal conditions under tested tunnels in sweet pepper cultivation resulted in growth decrease

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and differences in plant foliage [1]. Light access can be also limited by using additional layers of chalk and milk solutions on the tunnels' surface. Covering tunnels with extra layer of ethylene vinyl acetate film (EVA) decreased PAR transmission by 5 % and with polypropylene textile (PP) by 8 % [2]. Losses of light reaching 60 % were shown when cover made from polyester was stretched over plants [3]. In vegetable production deficit of light usually leads to yield decrease [2, 4, 5]. Initial experiments conducted in 2004 with shading celery shown that light limitation caused by black film clearly decrease dry matter and assimilation dyes content in plants [5].

The main objective of the study was to determine the effect of shading celery and butterhead lettuce with different solar permeability films on vegetative growth, marketable yield and some factors of yield quality.

Material and methods

All polyethylene films of original and recycled materials were manufactured by 'Jagapol' Film Manufacturing Facility in Krakow with the use of blow molding technology. Original films were made of Basell Orlen Polyolefins material and recycled films of high quality material originating from waste products supplied by Gumiplast company. As colouring agents white (Schulman 8160) and black (Polibatch black 1850) dyes were used.

Field experiments were conducted at Experimental Station of University of Agriculture in Krakow (Mydlniki) in 2005–2007. Trials were carried out on brown soil. After harvesting barley, field was first fertilized with phosphorus and potassium according to soil analyses and then ploughed. In the autumn of each year (2004, 2005 and 2006), the field was fertilized with 35 $Mg \cdot ha^{-1}$ manure, 100 kg $P_2O_5 \cdot ha^{-1}$ (triple superphosphate) and 200 kg $K_2O \cdot ha^{-1}$ (potassium chloride). In the spring, prior to planting, the field was fertilized with nitrogen, in doses of 50, 75 and 50 kg $N \cdot ha^{-1}$ (nitro-chalk). After the planting, only celeries were subjected to fertilization with ammonium nitrate in the dose 20 kg $N \cdot m^{-2}$, following that 0.1 % lime saltpetre (2 $dm^3 \cdot m^{-2}$) were used.

The work concerned a very early 'Melodion' cv. butterhead lettuce and medium-early celery 'Tango' cv. of intensively green leaves. Experiments with lettuce were carried in 2005 and 2006, with celery additionally in 2007 (due to difficulties with the interpretation of two-year results).

Lettuce seeds were sown into greenhouse on 2 March both years of the experiment. Transplants were planted on 7 April 2005 and 11 April 2006, respectively. Lettuce was harvested each year on 30 May. Celery seeds were sown on 4 February 2005, 5 February 2006 and 6 February 2007. Transplants with 4 leaves were planted on 17, 19 and 20 April and the harvest was carried out on 5, 11 and 13 July, respectively. Transplants of both species were planted into the field in 30 × 25 cm distance. Experimental plots, each of 3 m^2 (40 plants) were established in randomized blocks with four replications.

Shadings (0.1 mm thick and 2.4 m width) were fixed on the tunnel structure of 1.5 (width) × 1 m (height) × 10 m (length) and to assure air circulation in tunnels film reached only to 30 cm above soil surface. Lettuce was shading a week before harvest (23 May 2005 and 25 May 2006, respectively) and celery 10–12 days before harvest (29 June 2005, 1 July 2006 and 25 June 2007, respectively).

Treatments were made by various kinds of films used in shading:

1. control (without film),
2. transparent film from original material,
3. transparent film from recycled material,
4. white film from original material,
5. white film from recycled material,
6. black film from original material,
7. black film from recycled material.

Yield was determined in the area of 1 m^2 based on four replications including standards for celery: PN-R-75512 and butter lettuce PN-R-7522.

In order to determine dry matter content, samples of plant material were dried at 92–95 ^{o}C, total sugars were determined using antrone reagent method and L-ascorbic acid with Tillman's method. Results were processed statistically with Newmann-Keuls test, using STATISTICA program at a significance level of $p = 0.05$.

Results and discussion

As shown earlier [5], the transmittance of radiation through PE film differed considerably. The laboratory measurements indicated that the transmittance of radiation within the ranges of $\lambda = 400–700$ nm and $\chi = 700–1100$ nm differed depending on the tested cover. The highest transmittance was through transparent film: 87.1 % and 86.2 % in the above ranges, respectively. White film had very low transmission within these ranges (21.2 % and 33.6 %, respectively) and black film did not let the radiation at all [5].

The measurements of morphological parameters of plants showed a significant effect of shadings on the vegetative growth of celery. Shading in final cultivation stage caused that celery grown under white film, in all three years of the experiment, were higher than other ones (Table 1). Plants grown under black film – where access of light was very low – were not much higher than control plants. Similar dependence was demonstrated with the length of the stalks. No differences in number of leaves were observed. No statistically important differences were shown in the growth of celery cultivated under films made from recycled and original materials.

In relation to yielding in 2005 best effect was obtained under white film, in the next year under transparent and white film and in the last year of the experiment the yield was even in all objects with small advantage under white film (Table 2). Mean values indicated that increase of marketable yield was obtained when shading with white and transparent films were used. It was shown that black film decreased growth and yield, which was smaller than the yield obtained from the control. No differences were shown in the yield of celery cultivated under films made from recycled and original materials.

In sweet pepper production coloured non-woven limited solar radiation considerably and reduced soil temperature which resulted in differences in vegetative growth, poorer

Table 1

The effect of kind of plastic film used for shadings on the growth of celery in 2005–2007

Kind of plastic film	2005			2006			2007			Mean 2005–2007		
	Height of plant [cm]	Length of stalk [cm]	Number of stalks per plant	Height of plant [cm]	Length of stalk [cm]	Number of stalks per plant	Height of plant [cm]	Length of stalk [cm]	Number of stalks per plant	Height of plant [cm]	Length of stalk [cm]	Number of stalks per plant
Control (without film)	51.4 aA [2]	25.5 bA	10.0 abA	41.2 aA	17.5 aA	10.4 a	47.4 aA	25.3 abA	9.8 aA	46.7	22.8	10.0
Transparent original	58.3 cd	27.3 bc	9.5 a	53.5 c	22.4 b	12.3 b	50.5 a	24.8 ab	10.5 a	54.1	24.8	10.8
Transparent recycled	56.2 bc	26.6 bc	9.5 a	52.3 c	21.7 b	12.4 b	46.6 a	26.0 ab	9.8 a	51.7	24.8	10.6
Mea for transparent	57.2 B	26.9 B	9.5 A	52.9 C	22.0 B	12.3 B	48.5 A	25.4 B	10.2 A	52.9	24.8	10.7
White original	58.3 cd	28.1 c	9.6 a	58.0 d	21.7 b	12.4 b	55.2 b	26.8 b	10.5 a	57.2	25.5	10.8
White recycled	60.2 d	27.8 bc	10.1ab	54.2 c	23.0 b	12.7 b	55.4 b	26.2 ab	10.0 a	56.6	25.7	10.9
Mean for white	59.2 B	27.9 B	9.8 AB	56.1 D	22.3 B	12.5 B	55.3 B	26.5 B	10.2 A	56.9	25.6	10.8
Black original	49.7 a	23.1 a	10.3 b	46.6 b	18.6 a	11.7 ab	47.4 a	23.7 a	10.2 a	47.9	21.8	10.7
Black recycled	54.9 b	25.9 bc	10.3 b	46.5 b	18.0 a	12.5 b	48.0 a	23.4 a	10.5 a	49.8	22.4	11.1
Mean for black	52.3 A	24.5 A	10.3 B	46.5 B	18.3 A	12.1 B	47.7 A	23.6 A	10.4 A	48.8	22.1	10.9
Original [1]	55.4 X	26.2 X	9.8 X	52.7 X	20.9 X	12.1 X	50.1 X	25.2 X	10.3 X	52.7	24.1	10.7
Recycled [1]	57.1 X	26.8 X	10.0 X	51.0 X	20.9 X	12.5 X	49.4 X	25.2 X	10.1 X	52.5	24.3	10.9

[1] Means for the film material; [2] Statistical analysis concerns each year separately; values designated with the same letters do not differ significantly; small letters concern interaction material x color of film, capital letters – color of film, X, Y – the film material.

Table 2

The effect of kind of plastic film used for shadings on the marketable yield of celery $[kg \cdot m^{-2}]$ in 2005–2007

Kind of film	2005			2006			2007			Mean for stalks + blades
	stalks	blades	stalks + blades	stalks	blades	stalks + blades	stalks	blades	stalks + blades	
Control (without film)	2.72 abA[2]	1.71aA	4.43 abA	3.41 abA	2.19 aA	5.60 aA	4.25 aA	2.36 aB	6.62 aA	5.55
Transparent original	2.31 a	1.64 a	3.95 a	4.61 b	2.54 a	7.15 a	4.29 a	2.14 a	6.44 a	5.85
Transparent recycled	2.86 ab	1.82 ab	4.68 b	4.02 ab	2.33 a	6.34 a	4.10 a	2.01 a	6.11 a	5.71
Mean for transparent	2.58 A	1.73 A	4..31 A	4.31 B	2.43 A	6.75 B	4.20 A	2.08 AB	6.27 A	5.78
White original	2.91 ab	1.90 b	4.81 b	4.12 ab	2.38 a	6.50 a	4.44 a	2.16 a	6.61 a	5.97
White recycled	3.60 b	1.79 ab	5.39 c	3.62 ab	2.38 a	6.00 a	4.84 a	2.23 a	7.08 a	6.16
Mean for white	3.25 B	1.85 B	5.10 B	3.87 AB	2.38 A	6.25 AB	4.64 A	2.20 AB	6.84 A	6.06
Black original	2.72 a	1.35 a	4.07 a	3.27 a	2.21 a	5.47 a	4.30 a	1.96 a	6.26 a	5.27
Black recycled	2.43 a	1.41 a	3.84 a	3.45 ab	2.08 a	5.53 a	4.30 a	1.96 a	6.26 a	5.21
Mean for black	2.57 A	1.38 A	3.95 A	3.36 A	2.14 A	5.50 A	4.30 A	1.96 A	6.26 A	5.23
Original[1]	2.65 X	1.63 X	4.28 X	4.00 X	2.38 X	6.37 X	4.34 X	2.09 X	6.44 X	5.70
Recycled[1]	2.96 X	1.67 X	4.64 X	3.70 X	2.26 X	5.96 X	4.41X	2.07 X	6.48 X	5.69

Explanation: as in Table 1.

foliage and losses flower and fruit sets. The microclimate conditions under tested covers affected the yield significantly. The early yield under tunnels covered with PE films was considerably higher than under non-woven tunnels. When air temperature was high plants grown under non-woven covers had better growing and yielding conditions. Here the radiation and thermal conditions were much better which resulted in better and higher yield [1]. Lower yield, delay in growth and development as a result of shading were obtained in cucumber [2], pepper [3] and tomato [4]. In presented experiment deficit of light under black film resulted in smaller plants and shorter stalks of celery than these obtained from transparent and white film (Table 2). The single plant weight decreased simultaneously with the decrease of PAR permeability through films. Plant weight and length of stalks were significantly higher under transparent and white film in comparison with control.

Preharvest plant shading significantly modified some factors of biological value in stalks (Table 3). In the first two years of the experiment the highest content of ascorbic acid and dry matter was found in control plants, and in the last year of the experiment in the stalks grown under transparent film. Celery cultivated under transparent film had the highest content of soluble sugars in 2007 and in the year before. Shading with black film regardless of the material the film was made from, caused a significant decrease of ascorbic acid, dry matter and soluble sugars content.

Shading lettuce during 7 days before harvest with different coloured films demonstrated that yield depended on light permeability through shadings (Table 4). In 2005 great difference between yield obtained from control and from shading plants was observed. Because of the cool spring that year all shadings increased mast of plants. The highest marketable yield was obtained from stands shading with white and transparent film. Significantly higher was also yield from black film in comparison with the control. In the following year, similar tendencies were observed particularly in the case of transparent film. Significantly lower yield was obtained from lettuce grown under black film. Mean values from two years of the experiment show that the main cause for the obtained dependences is the inducting effect of light on lettuce's mass. Bad light conditions even for a short period of time can significantly decrease yield. The type of material the film was made from had no effect on yielding. Similar dependences were observed as far as the content of soluble sugars in butterhead lettuce is concerned. The highest content of soluble sugars was found in control and in plants grown under transparent film, the lowest in plants from black film. The content of ascorbic acid was changeable in each object only in 2005 small differences have been shown in plants grown under black and white films in relation to other treatments. This fact might have been connected with plants' reaction to light stress. The highest content of dry matter in 2005 was demonstrated in plants grown under transparent film and in the following year under white film and in non-covered plants. The kind of material shading films were made from had no significant effect on ascorbic acid and dry matter content in lettuce leaves. It was demonstrated that in the second year of the experiment the content of soluble sugars was slightly modified by the kind of materials from which films were made.

Table 3

The effect of kind of plastic film used for shading on ascorbic acid, soluble sugars, and dry matter content in celery stalks in 2005–2007

Kind of film	Ascorbic acid [mg · 100 g^{-1} f.m.]			Soluble sugars [mg · 100 g^{-1} f.m.]			Dry matter [%]		
	2005	2006	2007	2005	2006	2007	2005	2006	2007
Control (without film)	10.47 eC [2]	18.20 dD	13.10 dC	0.90 eD	1.37 bC	1.31 cdB	6.01 dC	9.50 dD	7.73 cC
Transparent original	9.10 d	12.63 bc	14.03 e	0.84 d	1.55 c	1.64 f	5.42 c	7.03 c	8.51 e
Transparent recycled	8.70 d	13.07 c	13.10 d	0.79 d	1.79 d	1.54 e	5.33 c	7.02 c	7.99 d
Mean for transparent	8.90 B	12.85 C	13.57 D	0.81 C	1.67 D	1.59 C	5.37 B	7.02 C	8.25 D
White original	8.00 c	10.10 a	11.00 c	0.69 c	0.97 a	1.37 d	4.61 b	5.16 a	6.81 b
White recycled	7.30 b	12.20 b	10.53 c	0.67 c	1.63 c	1.22 c	4.72 b	7.01 c	6.76 b
Mean for white	7.60 A	11.15 B	10.77 B	0.68 B	1.30 B	1.30 B	4.66 A	6.09 B	6.78 B
Black original	8.90 d	9.50 a	6.43 a	0.61 b	0.94 a	0.69 a	4.78 a	5.45 ab	5.30 a
Black recycled	6.23 a	9.90 a	7.37 b	0.49 a	0.94 a	0.79 b	4.93 a	5.89 b	5.32 a
Mean for black	7.56 A	9.70 A	6.90 A	0.55 A	0.94 A	0.74 A	4.52 A	5.67 A	5.31 A
Original [1]	8.67 Y	12.60 X	11.14 X	0.71 X	1.21 X	1.25 X	4.78 X	6.78 X	7.09 Y
Recycled [1]	7.41 X	13.34 Y	11.02 X	0.65 X	1.43 Y	1.22 X	4.93 X	7.35 Y	6.95 X

Explanation: as in Table 1.

Table 4

The effect of kind of plastic film used for shading on the yield and content of some quality indices in lettuce leaves in 2005–2006

Kind of film	Yield [kg · m^{-2}]			Soluble sugars [%]		Ascorbic acid [mg · 100 g^{-1} f.m.]		Dry matter [%]	
	2005	2006	Mean	2005	2006	2005	2006	2005	2006
Control (without film)	2.35 aA[2]	5.13 abB	3.74	1.14 bB3	1.08 bC	25.70 dC	19.63 bcA	4.74 eB	5.38 cC
Transparent original	4.74 b	6.26 c	5.50	1.27 b	1.25 c	20.26 c	16.40 a	4.79 e	4.69 a
Transparent recycled	4.16 b	6.12 c	5.14	1.22 b	1.10 b	18.50 bc	21.00 c	5.23 f	5.08 b
Mean for transparent	4.45 C	6.19 C	5.32	1.24 B	1.17 D	19.38 C	18.68 A	5.01 C	4.87 A
White original	4.54 b	4.74 a	4.64	0.81 ab	1.07 b	15.33 a	20.07 bc	3.98 b	5.88 d
White recycled	4.27 b	5.73 bc	5.00	0.50 a	0.76 a	16.70 ab	19.60 bc	4.33 c	5.16 b
Mean for white	4.41 C	5.24 B	4.82	0.65 A	0.92 B	16.01 A	19.83 A	4.15 A	5.52 D
Black original	3.09 a	4.29 a	3.69	0.58 a	0.71 a	17.60 b	20.07 bc	3.75 a	5.10 b
Black recycled	3.07 a	4.72 a	3.89	0.85 ab	0.73 a	17.59 b	17.80 ab	4.52 d	5.34 c
Mean for black	3.08 B	4.50 A	3.79	0.71 A	0.72 A	17.59 B	18.25 A	4.13 A	5.22 B
Original [1]	3.68 X	5.11 X	4.39	0.89 X	1.03 Y	17.73 X	18.70 X	4.17 X	5.26 X
Recycled [1]	3.47 X	5.44 Y	4.45	0.86 X	0.92 X	17.59 X	19.50 X	4.69 X	5.24 X

Explanation: as in Table 1.

Conclusions

1. The best elongation growth of celery was shown under white film which also slightly increased the yield of celery stalks.

2. Shading lettuce with transparent film for 7 days before harvest increased the yield and soluble sugars content in plants.

3. In celery and in butterhead lettuce with the decrease of PAR permeability through films content of dry matter, soluble sugars and ascorbic acid in general also decreased.

4. No differences were shown in the growth, quality and yield of celery and lettuce grown under films made from original and recycled materials.

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WPŁYW CIENIOWANIA FOLIĄ O RÓŻNYM ZABARWIENIU NA PLON I JAKOŚĆ SELERÓW NACIOWYCH ORAZ SAŁATY MASŁOWEJ

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Abstrakt: W latach 2005–2007 wykonano w Uniwersytecie Rolniczym w Krakowie doświadczenia polowe z cieniowaniem folią polietylenową roślin selerów naciowych odm. 'Tango' i sałaty masłowej odm. 'Melodion'. Cieniowanie folią bezbarwną, białą i czarną, wyprodukowaną z surowców oryginalnych i recyklingowych w przypadku sałaty wykonywano na tydzień przed zbiorem (odpowiednio od 23.05.2005 r. i 23.05.2006 r.), a w przypadku selerów 10–12 dni przed zbiorem (odpowiednio od 29.06.2005 r., 1.07.2006 r. i 25.06.2007 r.).

Wzrost elongacyjny selera naciowego był najsilniejszy pod folią białą, która powodowała także nieznaczne zwiększenie plonu ogonków liściowych. Pod względem plonowania w 2005 r. najlepszy wynik uzyskano pod folią białą, w kolejnym pod bezbarwną i białą, a w ostatnim plon był wyrównany we wszystkich obiektach, z niewielką przewagą obiektów, w których stosowano folię białą. Cieniowanie roślin sałaty bezbarwną folią na tydzień przed zbiorem spowodowało wzrost plonu oraz zawartości cukrów rozpuszczalnych. Wraz ze zmniejszaniem przepuszczalności folii dla promieniowania fotosyntetycznie czynnego, zawartość suchej masy, cukrów i kwasu askorbinowego w selerach i sałacie zmniejszała się. Rodzaj surowca stosowanego do produkcji folii nie miał wpływu na wzrost, plonowanie i jakość selerów i sałaty.

Słowa kluczowe: sałata masłowa, seler naciowy, cieniowanie, folia polietylenowa, plon, jakość

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EFFECT OF THE PESTICIDE KARATE 025EC ON THE ANTIOXIDANT PROPERTIES OF RADISH (*Raphanus sativus* L.) SEEDLING EXTRACT

WPŁYW PREPARATU KARATE NA WYBRANE PARAMETRY STRESU OKSYDACYJNEGO W SIEWKACH RZODKIEWKI *Raphanus sativus* L.

Abstract: Radish (*Raphanus sativus* L.) seedlings are a recognized model organism used in short-term ecotoxicological tests, particularly in research on the toxicity of heavy metals, pesticides and xenobiotics. Radish seedlings were used to determine the toxicity of the pyrethroid Karate 025EC. In this study seeds of the Rowa variety of radish (*Raphanus sativus* L.) were germinated in Petri dishes lined with filter paper. The radish seedlings were grown under natural light conditions at a temperature of 22 °C, with no added nutrients. Samples for analysis were collected 2, 4, and 6 days after plating. Control samples were grown in the presence of water, while in the samples with Karate the pesticide solutions contained 0.005 % to 0.1 % of the active substance. The radish seedlings were shown to be sensitive to lambda-cyhalothrin, the active ingredient in Karate 025EC. The compound inhibited germination of the radish seeds, affected the morphology of the seedlings, and decreased germination energy and rate. The effect depended on the growth time and the concentration of the active substance. Water extracts were prepared from the seedlings that had been subjected to the activity of lambda-cyhalothrin and their antioxidant activity was determined by a modification of the method of Brand-Williams et al, using the synthetic radical DPPH (1,1-diphenyl-2-picrylhydrazyl). Total antioxidant activity based on reduction of the $ABTS^{\bullet+}$ cation radical was also determined, using the method of Re et al as modified by Bartosz. In the control, the total antioxidant activity of the extracts, determined both by the DPPH method and the ABTS method, decreased with growth time, possibly due to the seedlings rapid growth and utilization of reserve substances for the needs of the developing plant. In the samples grown in the presence of Karate 025EC the antioxidant content in the extract decreased more slowly, and inhibition of seedling growth was observed as well. A description of this phenomenon may be helpful in research on the toxicity of pyrethroids in radish seedlings used as a model organism.

Keywords: pyrethroid, *Raphanus* sp., total antioxidant capacity, ABTS, DPPH

Pyrethroids are crop protection chemicals with insecticidal properties. They block nicotinic acetylocholine receptors and gamma-aminobutyric acid receptors in the nerve cells of insects [1], causing hyperexcitation of the nervous system, irritation of

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respiratory muscles, and inhibition of the functions of the central respiratory centre, leading to the death of the insect [2]. These neurotoxins are characterized by strong insecticidal activity and relatively low toxicity for mammals; they show no tendency to accumulate in living organisms and are quickly metabolized and excreted. Nevertheless, the authors of many studies have emphasized that the mechanism of action of pyrethroids also involves the generation of free radicals, leading to non-specific effects on the cells of various organisms. Pyrethroids are esters of primary or secondary alcohols (containing at least one double bond) and chrysanthemic acid [2,2-dimethyl-3-(2-methylpropenyl)-cyclopropanecarboxylic acid], or halogen analogues of this acid [3]. For this study on the non-specific effects of pyrethroids, the commercial pesticide Karate 025EC, containing lambda-cyhalothrin, was selected. Various model organisms are used in ecotoxicological tests – microorganisms, nematodes, insects, fish, aquatic invertebrates, and various plant species. The model organism used in this study was radish (*Raphanus sativus* L.) seedlings, which are used in short-term ecotoxicological tests. Studies on the allelopathy mechanism [4] and changes in magnetic field intensity [5] as well as on the toxicity of heavy metals and pesticides [6, 7] have confirmed the usefulness of radish seedlings as a model organism. As germination is a vulnerable moment in plant development, seedlings are much more sensitive to environmental factors than fully developed adult plants.

Materials and methods

The commercial pyrethroid Karate 025 EC, containing lambda-cyhalothrin, was used for the experiments. Water solutions of the pesticide were prepared with 0.005, 0.01, 0.05, and 0.1 % lambda-cyhalothrin content. Seeds of the Rowa variety of radish (*Raphanus sativus* L.) were germinated on Petri dishes lined with filter paper, in natural light conditions, at a temperature of 22 ^{o}C, with no added nutrients [8].

Water extracts from the stems of the radish seedlings were prepared according to the method described by Zielinski and Kozlowska [9]. Determinations were made of total antioxidant capacity in the extracts based on reduction of the ABTS$^{\bullet+}$ cation radical using the method of Re et al as modified by Bartosz [10, 11], and of antioxidant activity based on properties of DPPH using the method of Brand-Williams et al, with modifications [12].

Determination of antioxidant activity using the ABTS method is based on the amount of reduced cation radical ABTS$^{\bullet+}$ produced beforehand in a reaction of ABTS with potassium persulfate. Identical volumes of the radish extracts were added to an ABTS$^{\bullet+}$ cation radical solution. When the antioxidants contained in the extract reduce the ABTS$^{\bullet+}$ cation radical to colourless ABTS, they cause the solution to lose its blue-green colour, with the decrease in intensity of the colour dependent on the antioxidant content in the sample [13]. Absorbance of the solution was measured 30 minutes after the reaction was initiated, at a wavelength of λ = 414 nm [11]. Antioxidant activity was calculated as a percentage of ABTS$^{\bullet+}$ cation radical inhibition using the following equation:

$$\% \text{ inhibition} = 100\ (A_0 - A_{avg.})/A_0\ [14]$$

where: $A_{avg.}$ – mean absorbance of the antioxidant solution being tested;
A_0 – absorbance of the radical solution.

The results were expressed as mmol of Trolox per 1 g f.m. of radish hypocotyls.

Using an equation analogous to the one in the method described above, the antioxidant activity of the extracts was calculated using the synthetic radical DPPH (1,1-diphenyl-2-picrylhydrazyl). Identical volumes of the radish extracts were added to an ethanol solution of DPPH. When DPPH reacts with an antioxidant, the stable DPPH radical takes on electrons from the antioxidant and loses its intense violet colour. The decrease in absorbance was measured in relation to the control sample (DPPH solution + ethanol) 30 minutes after the reaction was initiated at a wavelength of $\lambda = 517$ nm. Antioxidant content was expressed as mmol of Trolox per 1 g f.m.

All determinations were made in at least three independent replications.

Results and discussion

Karate 025 EC inhibits germination and growth of radish seedlings. This effect increased with growth time and depended on the concentration of lambda-cyhalothrin. Because necrotic changes in the radicles were also observed in the plants grown in the presence of higher pyrethroid concentrations, extracts were made from seedling stems with cotyledons. On the fourth day of growth the length of the hypocotyls growing in the presence of the pyrethroid was 16.5, 11.00, 6.70 and 2.20 mm for lambda-cyhalothrin concentrations of 0.005 %, 0.01 %, 0.05 %, and 0.1 %, respectively, compared with the control. The pyrethroid pesticide Cyperkill Super 025EC containing cypermethrin had a similar effect on radish seedlings, reducing germination energy and rate [7]. Radish seedlings are often used in ecotoxicological tests because they are sensitive to various environmental factors. Diamines in concentrations from 0.02 to 0.1 % have been shown to reduce the number of germinating radish seeds [15]. The pesticide 1,2,3,4,5,6-hexachlorocyclohexane (HCH), a chlorinated hydrocarbon, has been found to inhibit growth of radish seedlings [16]. A common manifestation of the phytotoxic effects of various compounds is a decrease in biomass, which was confirmed by Wieczorek in his study on the effect of anthracene on radish seedlings [17].

Apart from their characteristic insecticidal activity, pyrethroids also generate free radicals, leading to symptoms typical of oxidative stress. In studies on the non-specific effects of pyrethroids on various organisms, determinations are often made of such markers of oxidative stress as antioxidant concentration, activity of catalase, superoxide dismutase, and glutathione preoxidase, and lipid peroxidation level. Enzymatic and non-enzymatic cellular protection mechanisms prevent uncontrolled oxidation reactions, particularly free radical reactions. A number of methods are known for determining total antioxidant capacity, understood as the capability of the material tested to counteract a given oxidation reaction. The measurement methods employed in this study, using ABTS and DPPH, enable determination of the total antioxidant capacity of radish hypocotyl extracts.

The methods using the reagents DPPH and ABTS are widely employed for measuring the antioxidant activity of plant extracts, food products [18] and systemic fluids [11]. These methods are often used in determining the antioxidant properties of phenol compounds [19].

When the ABTS method was employed, the total antioxidant capacity of extracts from the two-day radish hypocotyls in the control sample was found to be characterized by high content of antioxidant substances and was equivalent to 98.93 mmol of Trolox (Table 1). In the control samples total antioxidant capacity decreased with the time of the experiment. In 4-day hypocotyls the content of antioxidant substances decreased to about 77 %, and in the 6-day seedlings it was 52 % compared with the 2-day control samples (Table 1). The results obtained when antioxidant properties were measured by the DPPH method also suggest that antioxidant content in the extract decreases during seedling development (Table 1). Antioxidant activity in the extracts from the second day of growth was equivalent to 77.69 mmol of Trolox, while on days 4 and 6 these values were 47.15 and 30.88 mmol of Trolox, respectively.

Table 1

The effect of Karate 025EC on antioxidant properties of extract of radish (*Raphanus sativus* L.) seedlings

Time [day]	Lambda-cyhalothrin concentration [%]				
	0	0.005	0.01	0.05	0.1
Hypocotyl length of radish seedlings [mm]					
4	16.5 (± 6.20)	16.5 (± 4.22)	11.00 (± 5.98)	6.70 (± 3.83)	2.20 (± 2.57)
6	25.50 (± 7.86)	18.40 (± 4.97)	14.40 (± 6.77)	2.10 (± 3.57)	0.2 (± 0.42)
Antioxidant properties of the extract measured by the DPPH method [mmol trolox · g^{-1}]					
2	77.69 (± 9.40)	84.98 (± 5.72)	87.56 (± 7.20)	96.97 (± 3.92)	88.45 (± 6.94)
4	47.15 (± 4.31)	50.68 (± 2.20)	54.40 (± 3.28)	64.52 (± 1.96)	71.78 (± 2.24)
6	30.88 (± 2.56)	41.06 (± 4.94)	41.98 (± 7.94)	50.28 (± 10.96)	38.13 (± 6.08)
Antioxidant properties of the extract measured by the ABTS method of Re et al. [mmol trolox · g^{-1}]					
2	98.93 (± 11.45)	106.93 (± 9.81)	100.95 (± 10.02)	118.02 (± 5.31)	112.32 (± 5.98)
4	75.85 (± 5.39)	75.69 (± 4.90)	77.55 (± 4.33)	85.31 (± 7.56)	101.32 (± 6.52)
6	49.45 (± 5.74)	4.99 (± 9.52)	64.82 (± 13.19)	63,76 (± 17.65)	52.78 (± 10.09)

Measured by the DPPH method, the total antioxidant capacity (TAC) of the extract from the 2-day radish hypocotyls incubated with lambda-cyhalothrin was higher than in the control samples. The changes in total antioxidant capacity characteristic of the control were not found in plants germinating in the presence of the pyrethroid. On day 4 TAC was determined to be 152.23 % for the 0.1 % concentration of lambda-cyhalothrin, and for concentrations of 0.05, 0.01 and 0.005 %, up to about 136.84 %, 115.38 %, and 107.49 %, respectively, where 100 % was the control sample on that day. If we compare the TAC values between days 2 and 6 of growth, the difference (TAC on day 2 – TAC on day 6) is 50.32 for a 0.1 % concentration of lambda-cyhalothrin, and for concentrations of 0.05, 0.01 and 0.005 % it is 46.69, 45.58 and 43.92, respectively.

In the control sample the difference was 46.81. The difference in TAC between days 2 and 4 of growth (TAC on day 2 – TAC on day 4) for concentrations of 0.1, 0.05, 0.01 and 0.005 %, was 16.67, 32.45, 33.16 and 34.3, respectively. In the control sample the difference was 30.54.

In the control, total antioxidant capacity decreased with growth time. TAC of extracts from seedlings grown in the presence of the pyrethroid also decreased, but to a different degree than in the case of the control. When the highest concentration of the pyrethroid, 0.1 %, was used, a significant difference in TAC was observed between days 4 and 6 of growth (in the case of the DPPH method the difference between days 4 and 6 was 33.65 – far more than for other concentrations), while a slight difference was observed between days 2 and 4 of growth (with the DPPH method the difference was 16.67, significantly less than in the case of other concentrations). The changes were similar when the ABTS method was used. This high concentration of lambda-cyhalothrin caused the greatest inhibition of seedling growth, as well as necrotic changes.

The decrease in antioxidant content in the control samples may be due to the high rate of growth of the seedlings. Similar results were obtained when amaranth seedlings were grown; antioxidant content in the extracts decreased between days 4 and 7 of growth [20]. During germination, particularly in the catabolic phase, reserve substances are mobilized and utilized for the needs of the developing seedling [21]. Similar results were obtained in a study on the effect of another pyrethroid preparation, cypermethrin, on seedling development. In radish seedlings growing in the presence of cypermethrin the decrease in antioxidant content was found to take place more slowly than in the control, and cypermethrin also inhibited seedling growth [7]. A description of this phenomenon may be helpful in research on the toxicity of pyrethroids for radish seedlings used as a model organism.

Pyrethroids affect the antioxidant systems of the cells of various, often taxonomically diverse, organisms: microorganisms, invertebrates, mammals and plants. Changes in the functioning of the cellular antioxidant system are a sensitive indicator of oxidative stress induced by pyrethroids. The literature provides many experimental examples confirming this observation. A detailed discussion of this question can be found in several publications by this author [7, 22, 23].

Experiments conducted on *Saccharomyces cerevisiae* yeast have also confirmed that pyrethroids inhibit stress-induced biosynthesis of haemoproteins – catalase and cytochromes [7].

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WPŁYW PREPARATU KARATE NA WYBRANE PARAMETRY STRESU OKSYDACYJNEGO W SIEWKACH RZODKIEWKI *Raphanus sativus* L.

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Abstrakt: Siewki rzodkiewki (*Raphanus sativus* L.) to uznany organizm modelowy, który znalazł zastosowanie w krótkoterminowych testach ekotoksykologicznych, szczególnie w badaniach nad toksycznością metali ciężkich, pestycydów i ksenobiotyków. Siewki rzodkiewki posłużyły do określenia toksyczności preparatu z grupy pyretroidów Karate 025EC. W prezentowanej pracy kiełkowanie nasion rzodkiewki *Raphanus sativus* L. odmiany Rowa przeprowadzono na szalkach Petriego wyłożonych bibułą filtracyjną. Siewki rosły w naturalnych warunkach oświetlenia, w temperaturze 22 °C, bez dodatku składników odżywczych, próbki do analiz pobierano po 2, 4, 6 dniach od ich wysiewu. Próbki kontrolne rosły w obecności wody, w próbkach z preparatem Karate 025EC zastosowano wodne roztwory tego pestycydu o zawartości substancji aktywnej od 0,005 % do 0,1 %. Stwierdzono, że siewki rzodkiewki są wrażliwe na lambda-cyhalotrynę, aktywny składnik preparatu Karate 025EC. Związek ten hamował kiełkowanie nasion rzodkiewki, wpływał na morfologię siewek, obniżał energię i siłę kiełkowania, a efekt jego działania zależy od czasu hodowli i stężenia substancji aktywnej. Przygotowano wodne ekstrakty z siewek rzodkiewki poddanych działaniu lambda cyhalotryny i oznaczono w nich aktywność antyoksydacyjną według zmodyfikowanej metody Branda-Wiliamsa i współpracowników z użyciem syntetycznego rodnika DPPH (1,1-difenylo-2-pikrylohydrazyl). Całkowitą zdolność antyoksydacyjną opartą na zasadzie redukcji kationorodnika $ABTS^{\bullet+}$ oznaczono według metody Re i współpracowników w modyfikacji Bartosza. W kontroli w miarę czasu hodowli całkowita zdolność antyoksydacyjna ekstraktów oznaczana zarówno metodą z DPPH, jak i z ABTS zmniejsza się, co może być powiązane z intensywnym wzrostem siewek i wykorzystaniem substancji zapasowych dla potrzeb rozwijającej się rośliny. W próbkach rosnących w obecności preparatu Karate 025EC obniżanie się ilości antyoksydantów w ekstrakcie zachodzi wolniej, w próbkach tych stwierdzono też zahamowanie wzrostu siewek. Opis tego zjawiska może być pomocny w badaniach nad toksycznością pyretroidów na organizmie modelowym, jakim są siewki rzodkiewki.

Słowa kluczowe: pyretroidy, *Raphanus* sp., całkowita zdolność antyoksydacyjna, ABTS, DPPH

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MESOPHILIC ANAEROBIC DIGESTION OF PIG MANURE FOR BIOGAS PRODUCTION

FERMENTACJA METANOWA GNOJOWICY ŚWIŃSKIEJ W WARUNKACH MEZOFILNYCH

Abstract: The aim of the research was to establish the most appropriate technological parameters of anaerobic digestion treating non-straw-bedded pig manure. The digesters were maintained at a constant temperature of 36 ^{o}C (±0.5). The process was carried out at the following hydraulic retention times (HRT): 15, 18, 20, 23, 25, 30, 35 and 40 days. The applied range of HRT corresponds to the OLR value of between 1.18 and 3.13 kg VS/(m^3 · d). Both analyses of fermentation digestate, including the susceptibility to dewatering, as well as quantitative and qualitative biogas generated were carried out during the experiment. The criteria taken into account while assessing the applied HRT values included: biogas production rate, biogas yield, organic matter decomposition (VS and COD reduction) as well as stability indices (VFA; VFA/TA). It was established that anaerobic digestion of the analysed manure in conditions of high ammonia concentration (5760–6390 mg NH_4^+/dm^3) turned out to be stable and effective for the HRT value of between 25 and 35 days. When the HRT was reduced to below 25 days, a significant decrease in biogas production and deterioration in organic matter decomposition was noticed. Moreover, the VFA/alkalinity ratio exceeded 0.4; ie a value which is believed to cause instability in methanogens activity. The capillary section time (CST) measurement showed that the digestion process impacted the dewatering properties of the digested manure in a positive way.

Keywords: methane fermentation, renewable energy, biogas, animal by-products, swine manure

Animal breeding is strictly connected with generation of waste and by-products impacting on the natural environment. Animal rearing is either straw-bedded or non-straw-bedded, which determines the consistence and chemical composition of by-products generated. In the former case, the by-products are stall waste and liquid manure. Stall waste consists of animal faeces mixed with bedding material and a limited amount of urine. While liquid manure contains urine with a limited amount of water and stall waste leachate. Agricultural intensive production favours non-straw-bedded method.

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In this case, by-products constitute semi-liquid straw-bedded manure containing faeces, urine and fodder leftovers. Animal by-products, just like straw and harvest leftovers are treated as natural fertilizers and should be used predominantly for this purpose. Farms rearing animals on the massive scale (> 2000 animal standings for pigs weighted more than 30 kg or 750 standings for sows) are obliged to use at least 70 % of the manure generated as a natural fertilizers in their own arable land. The rest can be sold proving that it would also be used agriculturally. The manure which is not directly used as natural fertilizers is treated as waste and has to be neutralized [1, 2].

Natural fertilizers, including liquid animal by-products should be applied in the way which does not negatively affect the environment. According to the law [2, 3], maximum permissible dosages (45 m^3/ha) and application periods (1st March–30th November) should be strictly observed. Moreover, agrotechnical requirements and storage conditions should be met. Liquid manures should be stored in leak-proof containers with the capacity sufficient to keep the manure generated over a period of at least 4 months [3]. During storing animal excrements undergo natural biodegradation, which leads to the release of gases, mainly NH_3, CH_4, CO_2 and NO_x [4, 5]. Especially, ammonia released during excretion and storage is associated with agricultural activity. The ammonia release depends mainly on the amount of albumin compounds in fodder, pH, humidity as well as temperature [4, 6, 7]. It is estimated that in areas with high-intensity animal production about 70–80 % of the ammonia released comes from farming [4, 8]. Apart from releasing ammonia into the atmosphere, liquid manures leakages from storage tanks, may cause soil as well as surface and groundwaters degradation [4, 8, 9].

The methane fermentation generates a renewable energy in the form of biogas and digested manure in the form of stabilized natural fertilizer. Besides, the process ensures odour neutralization and has a positive impact on the separation of manure into liquid and solid fraction. The former can be utilized directly on the farm, while the latter can be easier transported into areas deficient in natural fertilizers [10, 11].

The aim of the research project was to establish the most appropriate technological parameters of anaerobic digestion of non-straw-bedded pig manure. The mesophilic digestion for biogas production was conducted at the *hydraulic retention times* (HRT) ranging from 15 to 40 days. The criteria taken into account while assessing the applied HRT values included: biogas production rate, biogas yield, organic matter biodegradation (VS and COD reduction) as well as process stability indices. Moreover, the influence of the digestion process on the dewatering properties of the digested manure was evaluated.

Materials and methods

In this experiment, pig liquid manure from a non-straw bedded rearing farm was used as a digestion feedstock. The samples were collected at the outlet of the pipe connecting animal standings with manure storage tanks. Table 1 presents the physical and chemical properties of the raw manure used.

Table 1

Characteristics of the digestion feedstock

Parameter	Unit	Raw manure	
		Range of variation	Average value
pH	—	6.62–7.32	6.89
ORP	mV	-90–-255	–170
BOD_5	g O_2/dm^3	23.5–26.0	24.4
COD	g O_2/dm^3	26.6–37.0	30.7
BOD_5/COD	—	0.70–0.88	0.79
Ammonia	g NH_4^+/dm^3	4.5–5.7	5.41
Phosphates	g PO_4/dm^3	1.32–1.57	1.49
Total solids (TS)	%	5.72–6.25	5.90
Volatile solids (VS)	%	4.58–4.92	4.71

The digestion was conducted in a bioreactor with a working volume of 3 dm^3. The digester was maintained at a constant temperature of 36 ^oC (±0.5). The process was carried out at the following hydraulic retention times (HRT): 15, 18, 20, 23, 25, 30, 35 and 40 days. The applied range of HRT corresponds to the *organic loading rate* (OLR) value of between 1.18 and 3.13 kg VS/(m^3 · d). The digesters contents were mixed periodically – 5 minutes in every 3 hours. Both analyses of the biogas produced as well as digested manure were carried out during the experiment. Chemical composition of the biogas produced was also periodically determined. The scope of the analyses conducted encompassed: pH value and ORP potential measurement as well as *total solids* (TS), *volatile solids* (VS), *chemical oxygen demand* (COD), *biochemical oxygen demand* (BOD_5), phosphates (PO_4^{3-}), *total volatile fatty acids* (VFA), *total alkalinity* (TA) and ammonium-nitrogen (NH_4^+) determinations. The susceptibility of the digested manure to separation into solid and liquid fraction was based on the *capillarity section time* (CST) [12–14].

Results and discussion

The process of methane fermentation was conducted under high ammonia concentration (5790–6390 mg NH_4^+/dm^3). The hydraulic retention time (HRT) of the manure in the bioreactor was gradually increased. Physical and chemical characteristics of the digested manure are presented in Table 2.

Firstly, the influence of the particular HRTs on the degrees of organic matter decomposition was taken into consideration. The process was initially adopted by the application of the shortest HRT value, ie 15 days, which was tantamount to 1.18 kg VS/(m^3 · d) of bioreactor *organic loading rate* (OLR). Anaerobic digestion for biogas production is a multi-step biochemical process, whereby macromolecular substances are converted into simpler compounds. The organic matter conversion can be expressed as a degree of volatile matter (VS) reduction or COD reduction – dissolved in supernatant, which is presented in Fig. 1. Under those conditions, the low reduction of VS, ie 25.2 %

Table 2

Physical and chemical properties of the digested manure

Parameter	Unit	HRT [days]							
		15	18	20	23	25	30	35	40
pH	—	7.44	7.51	7.59	7.60	7.85	7.90	7.93	7.95
TS	%	4.58	4.42	4.12	4.01	3.93	3.60	3.69	3.70
VS	%	3.52	3.41	3.14	2.96	2.88	2.58	2.72	2.71
COD	g O_2/dm^3	28.5	26.2	24.4	22.0	14.3	13.0	12.9	14.3
Ammonia	g NH_4^+/dm^3	6.39	6.21	5.94	5.88	5.79	5.81	5.92	5.89
VFA	g CH_3COOH/dm^3	7.54	7.38	7.25	5.17	3.80	3.15	3.47	3.79
TA	g $CaCO_3/dm^3$	12.3	12.4	12.3	12.0	12.2	13.7	13.6	14.3

as well as COD, ie 24.0 % was recorded. The HRT value was subsequently extended and the corresponding changes in VS and COD reduction recorded. The VS reduction increased gradually for the HRT ranging from 18 to 30 days. The maximal reduction of the VS – 45.2 % was achieved when the HRT was extended to 30 days, which was associated with an increase in OLR value to 1.57 kg /($m^3 \cdot d$). Further increase in HRT (35 days) did not have a positive impact on the parameter.

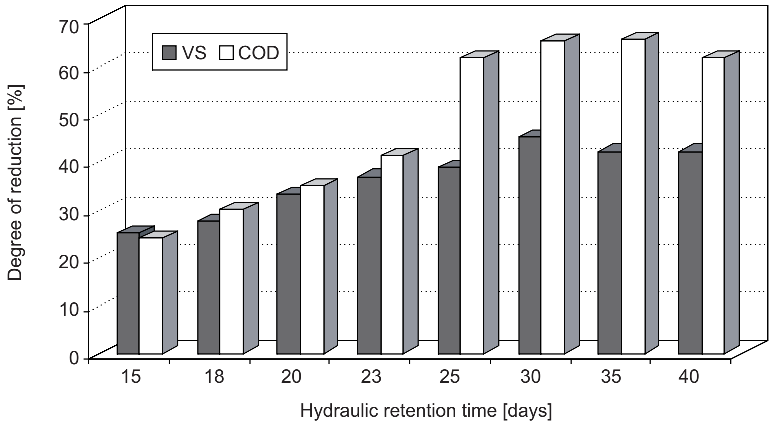

Fig. 1. The influence of hydraulic retention time (HRT) on the degree of organic matter decomposition

Just as in case of VS reduction, the degree of COD reduction increased up to the point where the HRT reached the level of 30 days. What is more, the most significant enhancement of the parameter occurred at the HRT of 25 days. In this case, the COD reduction amounted to 61.9 %. The maximum value of the parameter fluctuated around 65 % (65.3–65.6 %) and was recorded for the HRT in the range of 30–35 days. The application of the highest value of HRT (40 days) did not affect the organic matter bioconversion, expressed either in VS or COD reduction.

Secondly, the biogas production as well as methane content in the biogas generated was recorded. Figure 2 shows the amount of biogas produced for various HRT values, expressed in terms of daily production and biogas yield. Conducting the process for the HRT in the range of between 15–18 days, a relatively low daily biogas production (0.38–42 $dm^3/dm^3 \cdot d$) as well as biogas yield (0.16–0.18 $dm^3/g\ VS_{removed}$) was achieved. As the hydraulic retention time was extended (20–25 days), the daily biogas production (0.59–0.81 $dm^3/dm^3 \cdot d$) and biogas yield (0.26–0.37 $dm^3/g\ VS_{removed}$) increased gradually. When the HRT was increased to 30 days, the highest daily biogas production, ie 0,86 ($dm^3/dm^3 \cdot d$) was achieved, which is more than twice as in case of the amount of biogas generated for the initial range of HRT. Under those conditions, the biogas yield reached the value of 0.41 $dm^3/g\ VS_{removed.}$ The maximum value of biogas yield, ie 0.46 $dm^3/g\ VS_{removed}$ was received for the HRT of 35 days. Whilst the daily biogas production decreased slightly in those conditions (0.78 $dm^3/dm^3 \cdot d$). Similarly to the organic matter decomposition, the application of the highest HRT (40 days) did not play a positive influence on both biogas production indices.

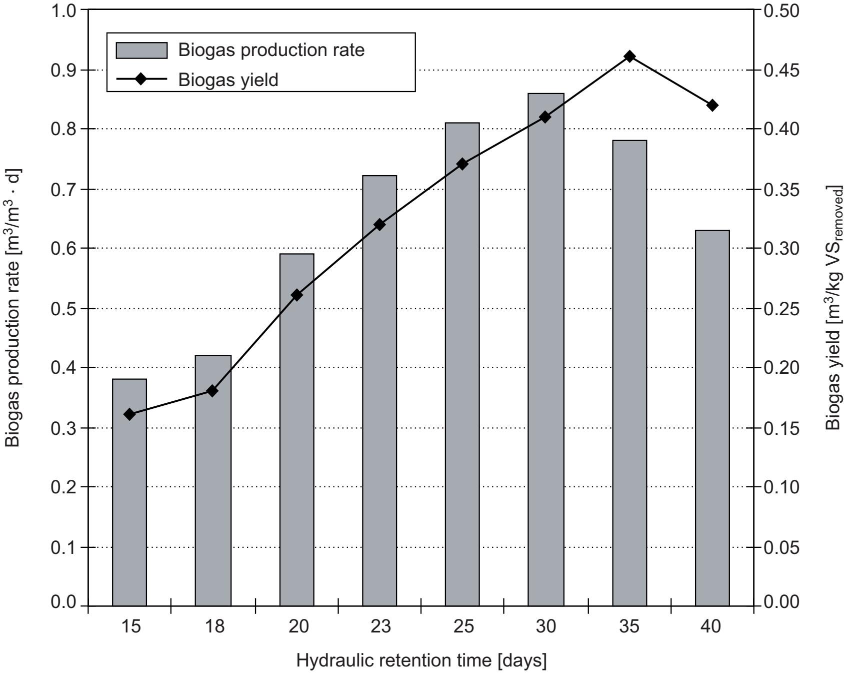

Fig. 2. Biogas production recorded during the experiment

The CH_4 concentration as well as several other biogas ingredients were analysed. The average methane content measured in a stable state of the process; for the HRT in the range of 18–40 days; fluctuated between 72 and 76 %. A high content of CH_4 was ascribed to the digestion feedstock rich in proteins, which are believed to produce biogas with the highest CH_4 content [15–16]. Whilst a relatively lower CH_4 content in biogas produced might have been a result of the lowest HRT applied (15 days). It turned out to be insufficient for effective methane fermentation in case of that type of feedstock.

Table 3

Chemical composition of the biogas produced

Ingredient	Unit	Hydraulic retention time [days]							
		15	18	20	23	25	30	35	40
CH_4	% vol.	65	72	74	76	74	75	76	75
CO_2	% vol.	30	23	22	20	21	20	21	20
O_2	% vol.	0.18	0.26	0.23	0.25	0.19	0.17	0.18	0.20
H_2S	ppm	62	81	12	11	12	10	14	10
CO	ppm	18	23	30	28	31	25	20	19

Thirdly, the influence of various HRT applied on the stability of the process was taken into account. One of the primary indicators which influences the biological conversion and microorganisms activity is the pH value. Microorganism consortia participating in anaerobic digestion tolerate the pH value in the range of between 5.5 and 8.5, however, the pH value should be maintained around the neutral level in order to ensure the appropriate growth and development of methane generating bacteria. Considering the digestion of animal by-products, the most important factors which determine the pH value and buffering capacity are: volatile fatty acids and ammonia nitrogen [17–19]. Generally, VFAs accumulation is responsible for a pH value drop. In our study, the highest VFAs concentration (5.17–7.54 mg CH_3COOH/dm^3) occurred for the HRT of between 15–23 days. When the process was conducted for the HRT above 23 days, the recorded VFAs concentration were more than twice lower (3.15–3.80 mg CH_3COOH/dm^3). The accumulation, which occurred was not related to a significant decrease in pH value (Table 2). The fact is not unexpected, mainly due to high concentration of protein in digested manure, which constitutes a potential source of ammonia nitrogen. On one hand, ammonia released counteracts the decrease of pH value caused by VFAs accumulation. On the other hand, if ammonia is released in excessive amounts, it causes the pH to increase above the value tolerated by most methanogens. The increase in pH can seriously depress the biogas generation or even caused it to stop completely. In our study, the concentration of ammonia nitrogen amounted to between 5.79–6.39 g NH_4^+/dm^3 (Table 2). A wide range of inhibiting ammonia concentrations has been reported in the literature – the value amounted to between 1.7 and 14 g/dm^3 [20]. What is more, methanogens have a tendency to acclimate to high ammonia concentrations.

Taking into account the fact that changes in pH value caused by VFAs accumulation in well-buffered processes; especially those containing high ammonia concentration; are often limited. Moreover, a significant decrease in pH value usually occurs after the collapse of the process and when the acid phase dominates in the bioreactor. A more reliable stability indicator seems to be a volatile fatty acids to total alkalinity, ie VFA/TA ratio. If the latter exceeds the threshold of 0.3–0.4, it is believed to have an inhibitive effect on the process stability [21–22]. The influence of the various HRT values on the VFAs accumulation and the VFA/TA ratio are shown in Fig. 3. On the basis of the above-mentioned ratio, we can figure out that the process exhibited stable conditions for the HRT higher than 23 days.

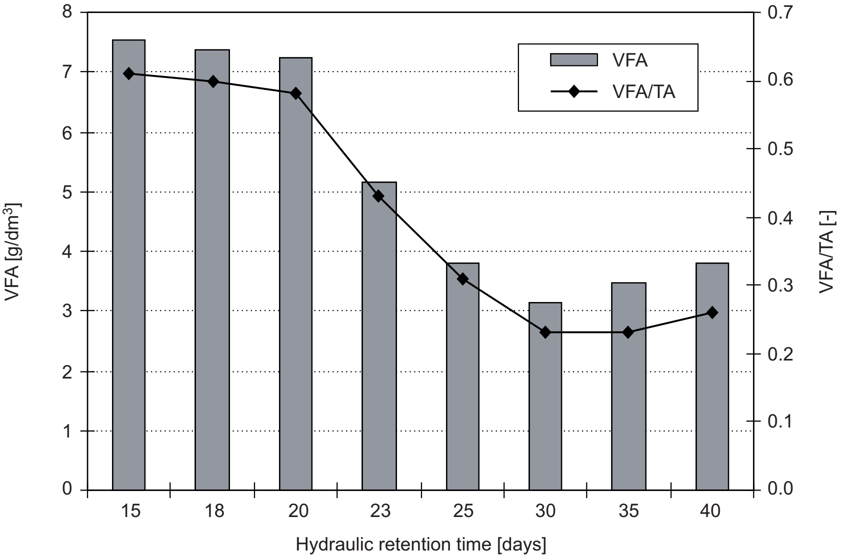

Fig. 3. The influence of various HRTs on the VFAs accumulation and VFA-TA ratio

Finally, the influence of methane fermentation on the dewatering properties of the digested manure was assessed. Digested manure constitutes a valuable natural fertilizer; however, in the areas of concentrated animal production; it is impossible to utilize the

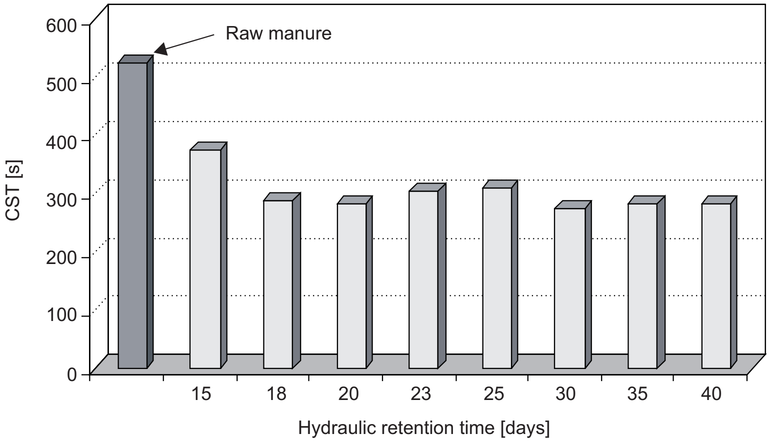

Fig. 4. Capillary suction time (CST) of both raw and digested manure

whole amount of manure generated for agricultural purposes. Therefore, in order to prevent the reverse influence of the unused portion of the manure on the natural environment, a reasonable solution seems to be the separation of the anaerobically digested manure into a solid and liquid fraction. The former can be used on the farm where it was generated, while, the latter can be transported more easily into areas deficient in natural fertilizers. Figure 4 shows the results of CST tests for both raw manure and digested manure. As compared with the raw manure (524 s), the digested manure exhibited a significantly lower value of the parameter (274–375 s). It may be concluded that the anaerobic digestion affects the separation properties of the digested manure in a positive way.

Conclusions

The research project allows to draw the following conclusions:

1. Taking into account environmental protection as well as the opportunity to produce renewable energy in the form of biogas, controlled anaerobic digestion of liquid animal by-products before its land application seems to be a reasonable solution.

2. The methane fermentation of the manure conducted under high ammonia concentration (5760–6390 $mgNH_4/dm^3$) turned out to be stable and effective for the HRT in the range of 25 and 35 days.

3. The highest biogas production (0.78–0.86 $dm^3/(dm^3 \cdot d)$) as well as the most appropriate degree of organic matter bioconversion (VS: 42.3–45.2 %; COD: 65.3–65.6 %) were achieved for the HRT of between 30 and 35 days, which was tantamount to OLR of 1.32–1.57 kg $VS/(m^3 \cdot d)$.

4. When the process was carried out for the HRT below 25 days, a significant decrease in biogas production as well as organic matter decomposition was recordeed. Moreover, the VFA/TA ratio increased above the critical value indicating instability in the process.

5. The anaerobic digestion affected the dewatering properties of the digested manure in a positive way.

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FERMENTACJA METANOWA GNOJOWICY ŚWIŃSKIEJ W WARUNKACH MEZOFILNYCH

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Abstrakt: Celem prezentowanych badań było ustalenie najkorzystniejszych parametrów technologicznych fermentacji metanowej gnojowicy świńskiej pochodzącej z hodowli trzody chlewnej. Fermentację prowadzono w warunkach mezofilnych 36 °C (±0,5) dla następujących wartości hydraulicznego czasu zatrzymania (HRT): 15, 18, 20, 23, 25, 30, 35 oraz 40 dni. Odpowiadały one obciążeniu komory bioreaktora ładunkiem suchej masy organicznej (s.m.o.) od 1,18 do 3,13 kg s.m.o./($m^3 \cdot d$). Podczas eksperymentu wykonywano analizy ilościowe i jakościowe generowanego biogazu oraz analizy fizykochemiczne materiału przefermentowanego. Dodatkowo analizowano wpływ fermentacji metanowej na właściwości odwadniające gnojowicy przefermentowanej. Analizując poszczególne wartości hydraulicznego czasu zatrzymania (HRT) gnojowicy w bioreaktorze, w głównej mierze wzięto pod uwagę: dobową oraz jednostkową produkcję biogazu, stopień biokonwersji materii organicznej oraz stabilność procesu (LKT; LKT/zasadowości). Fermentacja metanowa analizowanej gnojowicy prowadzona w warunkach dużego stężenia azotu amonowego (5760–6390 mg NH_4^+/dm^3) przebiegała stabilnie oraz efektywnie dla wartości HRT od 25 do 35 dni. W przypadku prowadzenia fermentacji metanowej dla wartości HRT poniżej 25, odnotowano znaczne zmniejszenie ilości generowanego biogazu oraz stopnia rozkładu materii organicznej. Stosunek LKT/zasadowości po tym czasie zatrzymania wzrósł powyżej 0,4, co świadczy o niestabilności procesu metanogenezy. Ponadto proces fermentacji metanowej wpłynął korzystnie na właściwości separacyjne przefermentowanej gnojowicy.

Słowa kluczowe: fermentacja metanowa, energia odnawialna, biogaz, odpady rolnicze, gnojowica świńska

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BIOFILM IN GRAVITATIONAL SEWER SYSTEM AND ITS INFLUENCE ON WASTEWATER BIODEGRADATION

BŁONA BIOLOGICZNA W KANALIZACJI GRAWITACYJNEJ I JEJ WPŁYW NA BIODEGRADACJĘ ŚCIEKÓW

Abstract: The biofilm layer developed on the wall of sewer pipes is a common formation in the natural environment. The biofilm can be defined as a natural accumulation of microorganisms on the solid body surface, like the pecton covering the surface of solid in the river water or the devices of the biological sewage treatment plant. The proportions of particular species in biofilm composition are different in various WWTPs or rivers due to the environmental condition influence. In the sanitation a fresh sewage is characterized by high concentration of pollutants in a form of organic compounds with particles of various properties and dimensions. It forms the environment rich in nourishment substrates available both for the biofilm and the suspended biomass. The biofilm in sewers is spatially strongly heterogeneous. It consists of caverns, channels and pores filled with liquids or gases depending on actual environmental conditions. It can be said that it is a potently diversified system, important in the biodegration of sewage in gravitational sewerage. Basing on the field and the literature examinations the authors will present the most important sewer biofilm parameters and their influence on the sewage biodegradation, as well as a basic model of this process.

Keywords: sewer biofilm, gravitational sewer systems, sewage biodegradation in sewer conduits

The biofilm layer developed on the walls of sewer pipes is a common formation in the natural environment. The biofilm can be defined as a natural accumulation of microorganisms on the solid body surface [1, 2], like the pecton covering the surface of solid in the river water or covering the devices of the biological sewage treatment plant [2–6]. The proportion of particular species in the biofilm composition are different in various places of *wastewater treatment plants* (WWTPs) or rivers due to the environmental condition influence. In the sanitation, a fresh sewage characterized by high concentration of pollutants in a form of organic compounds with particles of

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various properties and dimensions, forms the environment rich in nourishment substrates available both for the biofilm and the suspended biomass.

Biofilm consists of microorganisms embedded in a glycocalyx that is predominately composed of microbially produced exopolysaccharide (EPS) [1, 7]. But in the sewer system, biofilm also contains a large fraction of inorganic material eg zeolite, sand, etc, organic, like fats and higher species of saprobe microfauna which can have a significant impact on the biofilm properties (Fig. 1) [2, 3, 8].

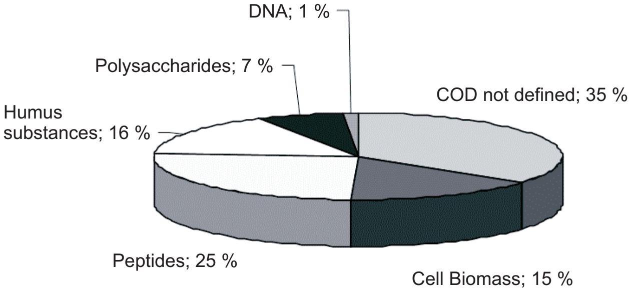

Fig. 1. Typical composition of biofilm in sewer system [2, 8]

The biofilm microorganisms develop the extracellular organic compounds enabling sedentary lifestyle. The mucus rich biofilm surface protects the microorganisms against washing away by the flowing sewage. It also stabilizes environmental conditions, prevents drying during the low filling of the conduits, and isolates from several chemical compounds and bacteriophages [2, 9–12]. The presence of biofilm considerably extends the mean residence time of heterotrophic biomass microorganisms inside the sanitation system. The development of significant populations of slower developing bacteria, such as sulfur reducing or executing methanogenesis is then possible [1, 2].

The population of bacteria existing inside the sanitation system is characterized by the ability to produce the innercellular spare materials – eg glycogen, which minimize the disparity in nutrients availability. It has a special significance inside the sanitation conduits of small diameter and high irregularity of sewage flow.

Biofilm structure

The fully developed biofilm is consisting of the characteristic layers [2, 13], determined by the availability of oxygen at the deeper located zones. The spatial variability of oxygenation results in the differences of structure properties, composition and transformation rate of chemical compounds inside the biofilm. The highly loaded biofilm contains, in the respective layers, the majority of microorganisms functional groups causing the pollutants biodegradation.

The spatial distribution of specific organisms groups defines the biological activity in the different zones of biofilm (Fig. 2). The research results show that the heterotrophic bacteria usually outnumber the autotrophic ones [2]. The heterotrophic bacteria spatial

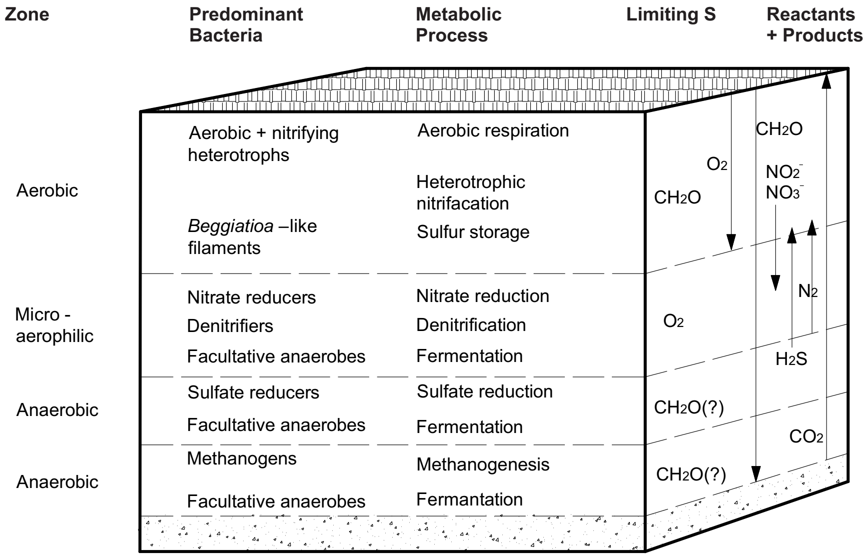

Fig. 2. The zones and processes in a typical stratified sewer biofilm [2]

distribution inside the biofilm is almost uniform, although the anaerobic facultative bacteria number increase from the level of 10^7–10^8 in deeper layers to 10^9–10^{10} CFU · cm^{-3} (CFU – *colonies forming units*) in the surface layer. The population of nitrifying bacteria sustains inside the sanitation biofilm at the level of 10^4–10^6 MPN · cm^{-3} (MPN – *most probably number*). It was proven that only about 25 % of all alive bacteria of surface layer is active metabolically in the real conditions, the rest remain inactive. Moreover, about 65 % of the whole biomass localized inside the biofilm in sanitation system forms the inert mass for biochemical transformations [2, 9].

The biofilm density increases along with the distance from the surface, from 14 kgTSS · m^{-3} (TSS – *total suspended solids*) in the surface zone to 97 kgTSS · m^{-3} in the deepest localized zone. The research shows that change in biofilm porosity also occurs, for the layers thicker than 500 μm, from 83–90 % for the surface layer to 67–64 % for the deepest layers [2]. The biofilm density also varies according to the location at wetted perimeter and increases, along with the height, from the sewage free surface to the bottom of the conduit.

The spatial distribution of prokaryotic microorganisms is also diversified by their rate of growth, because the faster developing groups usually cover the slower growing ones. Hence, the microorganisms of higher development rate accumulate near the surface of biofilm. According to the quantity of available nutrient substrate microorganisms inside the biofilm develop with different rate. Moreover, the prokaryotic organisms of biofilm are being permanently consumed by the eukaryotic heterotrophs.

The inner side of sanitation pipe walls is covered by the biofilm not only beneath but also above the wastewater free surface. This situation is connected to the frequent oscillation of sewage free surface level and also to the fact that nutrients may be transported by and consumed also directly from the humid air. It is clearly visible in locations of the turbulent flow – backdrop manholes or the other places of increased aerosols generation. Though, biofilm developed over the wastewater free surface is characterized by the noticeable lower oxygen activity than observed in case of the biofilm located beneath the surface. This difference is caused by the increased content of fat in the whole mass which, despite the decreased OUR activity (OUR – *oxygen uptake rate*), results in the increased resistance to erosion [2].

The biofilm developed inside the gravitational sanitation conduits reaches the thickness of, from a several, to over ten millimeters. The biofilm thickness changes and reaches its minimum at the high sewage flow velocity. The observed fibrous structures increase the process of oxygen consumption, thus reducing the oxygen uptake dependence from its concentration in the sewage [14, 15]. The numerous macro-pores, called "water channels" separated by the colonial organisms biomass are observed at biofilm surface of intensely irregular topography [13, 16]. The macro-pores facilitate mass transfer through biofilm then influencing the diffusion efficiency.

The exhaustive studies, describing the three dimensional processes of mass transport and biofilm development are not directly used in sewage biodegradation model. A number of expensive calibration measurements is required but the results quality may not clearly outperform the results of standard, less complicated models [13]. So the minimal number of input data, offering the satisfying results quality is required [1, 2, 11, 16]. This approach is illustrated in Fig. 3 containing the charts of real concentration changes of compounds dissolved in water, including the biofilm (left). The simplified form is also presented in Fig. 3 (right). Figure 3 presents also the boundary layer concentration for nitrates, influenced by nitrate usage in anoxic zone.

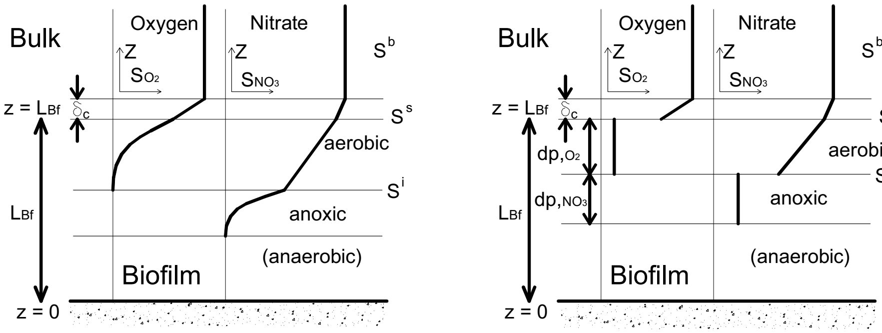

Fig. 3. A sketch of the boundary layer and the penetration depth, full model on the left and simplified one on the right [2, 8, 9]

Transformations of compounds containing biogenic substrates

The transformation processes of biogenic substrates occur inside the sanitation systems permanently or in the periodical pattern. But their influence on total pollutants load during the transport to WWTPs is limited.

The transformations of nitrogen may occur inside the biofilm layer – Fig. 4. However, the nitrifying bacteria quantity is usually about 1000 times smaller than the number of surrounding heterotrophic bacteria, hence nitrification inside the sanitation system plays only a minor role among the other biochemical processes. Denitrification inside biofilm occurs as along as nitrates originated from infiltration water are present. The nitrate presence in biofilm and wastewater does not affect the oxygen diffusion process in the biofilm [2]. Urea and protein hydrolysis are important sources of ammonium ion, thus considering the fact that these compounds are described by COD.

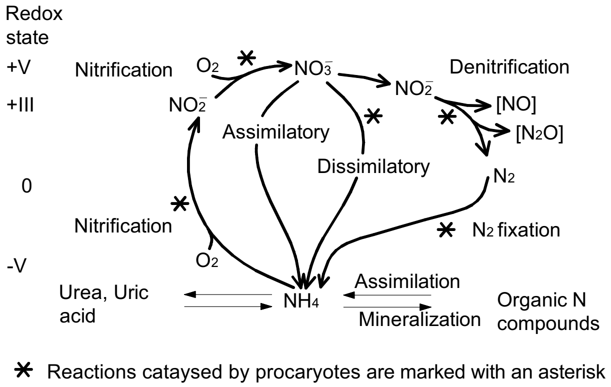

Fig. 4. Key reactions in the cycling of nitrogen species occurring in sewer system. The redox state of nitrogen is displayed on the left [2]

Figure 5 presents transformations of sulfur compounds in gravitational sanitation systems. The processes connected to the cycle of sulfur transformations result in pipes erosion and odour nuisance.

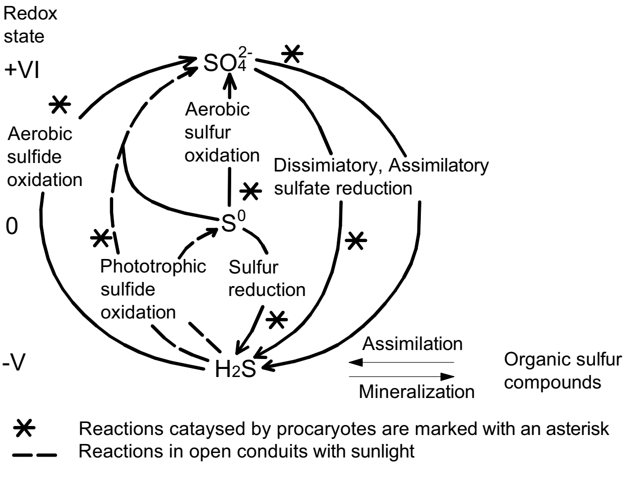

Fig. 5. Key reactions in the cycling of sulphuric species occurring in sewer system. The redox state of sulphur is displayed on the left, on the basis of [2, 8, 14]

Dynamic equilibrium of biofilm thickness

The biofilm thickness depends on the variety of different factors. The most important are: the growth of active cells biomass, accumulation of extracellular polymers and inert materials originated from the biomass dissolution as well as deposition of particles contained in sewage. The microorganisms biomass loss may be caused by the eukaryotic and prokaryotic organisms as well as the bacteriophages activity [2].

Erosion caused by the hydrodynamic effects of sewage flow results in a gradual but continuous biofilm mass loss. Abrasion and erosion causes the similar results. Shear stress at the level of 3–4 $N \cdot m^{-2}$ and above usually stops increase of biofilm depth on sanitation pipes walls. In case of pipes of diameter < 0.4 m, shear stress of given value appears at sewage flow velocity equal to about 1 $m \cdot s^{-1}$, for the pipes of larger diameter this velocity reaches the value of 1.2–1.4 $m \cdot s^{-1}$ [8].

The shear stress, after exceeding the limit value, causes periodical separation/erosion and transport of parts of biofilm downstream in a form of suspended biomass. This process may be supported by the internal transformations of the biofilm, resulting in decrease of strength of the layers of biofilm due to substrates or gases destroying the biofilm from inside [2].

All processes mentioned above together with the extreme events, like sudden uncontrolled flow with a high velocity or poisonous substances discharge, result in the reduction of the active biomass of biofilm. Atrophy of biofilm occurs also as a result of biomass extinction caused by deficiency of nutrients. As a final effect of these transformations, biodegradable substances immobilized inside biofilm are transformed to the soluble substrates by enzymes. The dissolved substrates may be used by biofilm organisms or diffuse outside the biofilm where they are transported by the stream of flowing sewage.

Biofilm dimensions, as it was reported in the literature [14], both, surface area and thickness depend on hydrodynamic conditions of flow inside sanitation pipes more than on biomass increase. The hydrodynamic conditions of flow are characterized by a high variability in time and length of the selected sanitation conduit. Moreover, flowing sewage stream generates shear stress of different values in different points of an active cross-section. The highest values are reached close to the pipe bottom and the lowest near the side walls close to the wastewater free surface. The abrasion forces caused by solid suspension drag are also very important in biofilm removal. Biofilm resistance to removal may be increased by fat settlement along the walls of sanitation pipe, it is especially important close to the free wastewater surface [2, 9, 10, 15, 17, 18].

Thus, the influence of velocity flow and shear stress on structure and properties of biofilm is evident [15]. It was proven during the laboratory studies at high values of shear stress when the eroded elements of biofilm caused biodegradation of available COD up to 80–90 % [14]. Up to 90 % of the whole biomass eroded by shear stress is being removed during the first 1–2 minutes of stress impact [2]. It was also observed that biofilm fragments separation declines after limiting the inflow of nutrients [2, 19]. The biofilm developed during the flow inducing shear stress of low value erodes significantly faster than biofilm developed in the environment of shear stress of high value. The highest biofilm accumulation may be, in turn, achieved at shear stress value about 1.5 N · m^{-2}. The rapid change of sewage flow velocity influence the mass transport and biofilm thickness while the long-lasting slow changes of the same amplitude result in biomass structure changes.

Modelling of biofilm influence on sewage biodegradation

The model presented below consists of two important processes: hydrolysis of suspended fractions and heterotrophic biomass growth in biofilm. Both are coupled with mass exchange terms. The research conducted *in situ* showed that biofilm is an important factor of transformation and biodegradation processes of pollutants in sanitation systems [2, 8, 20, 21]. In some specific cases its share in sewage biodegradation may be higher than the share of suspended biomass. This situation appears during the flow of low value shear stress and minor filling of the sanitation pipe. The internal biofilm processes application in a numerical model of sewage biodegradation allows to obtain the result comparable to the results obtained by models considering only the suspended biomass [4], with simultaneous possibility of decreasing the number of considered hydrolyzing fractions. The sewage temperature is a significant element of presented modeling description, it is important because it highly influences the enzymatic activity of microorganisms.

Hydrolysis

Considering the hydrolysis of n suspended fraction (each one hydrolyzes with different rate) in sewage, caused by enzymes of suspended biomass and biofilm in given temperature, the following equation describing the ρ intensity of this process may be written [8]:

$$\rho_{h,n} = k_{hn} \frac{X_{Sn} / X_{Bz}}{K_{Xn} + X_{Sn} / X_{Bz}} \frac{S_O}{K_O + S_O} \left(X_{Bz} + \varepsilon X_{Bf} \frac{A_{Bf}}{V} \right) \alpha^{(T-20)} \tag{1}$$

where: k_{hn} – hydrolysis rate constant for the n-th suspension fraction [d^{-1}],

K_{Xn} – saturation constant for the hydrolysis of n-th suspension fraction [gCOD · gCOD^{-1}],

X_{Sn} – concentration of n-th hydrolysable fraction [gCOD · m^{-3}],

X_{Bz} – heterotrophic active biomass in form of suspension [gCOD · m^{-3}],

X_{Bf} – heterotrophic active biomass in biofilm [gCOD · m^{-2}],

S_O – dissolved oxygen concentration [gO$_2$ · m^{-3}],

K_O – saturation constant for the dissolved oxygen [gO$_2$ · m^{-3}],

A_{Bf} / V – ratio of wetted surface of biofilm to sewage volume = R_h^{-1} [m^{-1}],

ε – constant of biomass efficiency [-],

α – temperature coefficient for processes in sewage [-],

T – temperature [^{o}C].

Heterotrophic biomass growth in biofilm

In order to describe the growth rate of heterotrophic biofilm biomass in aerobic conditions the deterministic model based on information presented in [8, 22] may be used:

$$\rho_f = k_{1/2}\, S_O^{1/2} \frac{Y_{Hf}}{1 - Y_{Hf}} \frac{S_S}{K_{sf} + S_S} \frac{A_{Bf}}{V} \alpha_f^{(T-20)} \tag{2}$$

where: $k_{1/2}$ – reaction rate constant of 1/2 power for surface usage of dissolved oxygen by biofilm [$gO_2^{1/2} \cdot m^{-1/2} \cdot d^{-1}$],
Y_{Hf} – efficiency rate for X_{Bf} (yield coefficient) [$gCOD \cdot gCOD^{-1}$],
K_{Sf} – saturation constant for biofilm dissolved biodegradable fraction [$gCOD \cdot m^{-3}$].

The knowledge of a minimal number of kinetics and stoichiometric factors is required to presented description of pollutant fraction hydrolysis rate and heterotrophic biofilm biomass development. But the presented model is not directly connected to the conduit hydraulics because the steady state of biofilm thickness is assumed.

Conclusions

The information presented above and the cited literature reports allow to draw the following conclusions concerning the composition, structure and biofilm preservation in different substrate load and variable shear stress:

– The fully developed, mature biofilm (older than 12 days) is more resistible to erosion than the younger biofilm.

– The amount of eroded biomass depends to the shear stress value.

– The amount of biomass removed from the biofilm by the increasing value of shear stress results from the conditions of biofilm development – the higher stress during the development phase causes more stable and resistible biofilm.

– The higher shear stress during the biofilm development results in its unequal spatial development.

– Sewer biofilm is a strongly diversified system playing an important role in sewage biodegradation process, but still not sufficiently recognized and described.

– The inner biofilm processes application in a numerical model of sewage biodegradation allows to obtain the results comparable with the results obtained by models considering only the suspended biomass, with simultaneous possibility of decreasing the number of considered hydrolyzing fractions.

– The significant element of presented modeling description is also the sewage temperature, important because it influences the enzymatic activity of saprobe microorganisms.

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BŁONA BIOLOGICZNA W KANALIZACJI GRAWITACYJNEJ I JEJ WPŁYW NA BIODEGRADACJĘ ŚCIEKÓW

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Abstrakt: Warstwa błony biologicznej narastająca na ściankach przewodów kanalizacyjnych jest formacją pospolicie występującą w środowisku naturalnym. Szeroką definicję błony biologicznej stanowi stwierdzenie, że jest to naturalna akumulacja mikroorganizmów na powierzchni ciała stałego. Przykładem może być chociażby pekton pokrywający przedmioty zanurzone w wodzie rzecznej, czy też biofilm porastający zanurzone w ściekach części urządzeń biologicznej oczyszczalni ścieków. Jednakże proporcje udziału poszczególnych gatunków w składzie biofilmu kanalizacyjnego są inne niż w oczyszczalniach czy rzekach, ze względu na różne warunki środowiskowe. W systemach kanalizacyjnych świeże ścieki charakteryzują się dużą koncentracją zanieczyszczeń w postaci związków organicznych o różnorodnych właściwościach oraz rozmiarach cząstek. Tworzy to środowisko życia mikroorganizmów bogate w składniki odżywcze, dostępne zarówno dla błony biologicznej, jak i biomasy zawieszonej. Błona biologiczna ma silnie heterogeniczną strukturę jakościowo-przestrzenną z licznymi zagłębieniami i porami wypełnionymi cieczą bądź gazem, w zależności od aktualnych warunków środowiskowych. Można więc stwierdzić, że jest mocno zróżnicowanym systemem, odgrywającym znaczącą rolę w procesach biodegradacji ścieków w kanalizacji grawitacyjnej. Korzystając z badań terenowych oraz literaturowych, autorzy prezentują najważniejsze właściwości biofilmu kanalizacyjnego, jego wpływ na biodegradację ścieków oraz podstawowe modele opisujące ten proces.

Słowa kluczowe: błona biologiczna, kanalizacja grawitacyjna, biodegradacja ścieków w kanalizacji

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EVALUATING THE EFFICIENCY OF SELECTED EXTRACTION METHODS FOR PAHs ON THE EXAMPLE OF COMPOST FROM URBAN WASTES

EFEKTYWNOŚĆ WYBRANYCH METOD EKSTRAKCJI PAHs (WWA) NA PRZYKŁADZIE KOMPOSTU Z ODPADÓW KOMUNALNYCH

Abstract: Extraction methods are especially important during the stage of preparing the samples to the identification and separation of the elements from environmental samples. Analytes, which are mainly solid organic substances, can be separated from solid materials either by a gas or a solvent. Nevertheless, solvents are still the most popular and the most widely used extractants. Still, the efficiency of extraction depends not only on the particular type of solvent but also on the extraction method. In literature, there are all sorts of assaying processes. Qualitative or quantitative persistent chemical pollutants are among others, polycyclic aromatic hydrocarbons (PAHs). This research was to test two different organic solvents, ie hexane, dichloromethane and hexane with acetone, as well as different extraction methods in the process of isolating polycyclic aromatic hydrocarbons from compost originating from municipal wastes.

Keywords: extraction, PAHs, compost

Polycyclic aromatic hydrocarbons, which represent persistent organic waste, have been rousing interest for over 100 years since their cancerous properties were discovered [1, 2]. The prevalence of these compounds requires a monitoring of their content in the environment [3]. They can be of natural or anthropogenic origin [4]. Due to their low concentration levels, it was necessary to apply effective methods of isolating, purification and inspissation.

One of the essential elements of analytical procedures, which are especially important in the analysis of environmental samples, is preparing research material for analysis. According to many authors, more than 60 % of the time of the overall analysis cost is preparing samples, while the actual analysis is less than 10 % of the overall cost. It is mainly due to the necessity of preliminary purification and isolation of the analysed

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substance from a complicated mixture containing different kinds of multiple molecules. This stage of preparing the samples is called purification. The selected method used to prepare environmental samples for analysis depends mostly on the element and sample properties as well as on the required detection limit, possibilities of the process, etc.

The most common techniques of purification, separation and inspissation in analytical chemistry are extraction techniques [2, 5].

Extraction is a method of separating and purificating compounds from a liquid or solid mixture by using appropriately selected selective solvents. The process is based on moving compounds contacting each other by phases: solid body-liquid or liquid-liquid.

Therefore, extraction allows:

- Separation,
- Separating interfering components,
- Inspissating (enriching) elements in trace analysis of high purity materials.

We can distinguish the following extraction techniques:

- liquid-liquid extraction (LLE),
- solid-phase extraction (SPE),
- superfcritical fluid extraction (SFE),
- solid-phase microextraction (SPME),
- single-drop microextraction (SDME),
- accelerated solvent extraction (ASE),
- ultrasound accelerated extraction (UAE) and
- microwave assisted extraction (MAE).

The most common methods used for separation and inspissation in analytical chemistry are solid body-liquid and solid phase extraction.

The most important issue connected with the extraction process is the choice of a particular solvent, which has to be characterised by the following features:

- Easiness of precipitation from the extract,
- The lowest possible mutual phase solubility,
- Favourable division ratio between the extractant and phase extractant,
- The highest possible difference between the solvent density and extractant phase,
- High surface tension.

Solid-liquid extraction is a versatile technique that allows a more effective separation of different substances from complex mixtures due to the possibility of using specific reagents allowing, as far as possible, a selective separation of the desirable compound.

Materials and methods

Compost used in the research was taken from the MPGU compost facility in Zabrze, Poland, where composting material is organic waste. The samples were taken on 3rd October 2007. Air-dried compost was used in the research. A fine fraction under 2 mm was examined. Samples with a mass of 10 g were used. The quality assessment of compost, based on trade norms were carried out as well. The study included:

- Determining the content of organic substances in compost from municipal waste (trade norm BN-88 9103-07),
- Determining the content of organic carbon (trade norm PN-91 Z-15005).

In order to isolate PAHs, samples of compost are put through the fexIKA vario control cycle for a period of 5 hours or in an ultrasonic bath (underwent sonication) for 30 minutes [5–7] (Fig. 1). Solvents quoted in the literature: hexane, dichloromethane and acetone/hexane, in a ratio of 1:1 by volume, were used in the process of extraction. In the chromatographic analysis, reagents with HPLC purity were used [1, 2, 8, 9].

The extract was obtained after a preliminary inspissation process in a stream of neutral gas, purified by aluminium oxide on a glass column (height = 12 cm, diameter = 0.5 cm) [5]. The column was stopped by a glass wool cork and was filled with dichloromethane and then was filled in turns with:

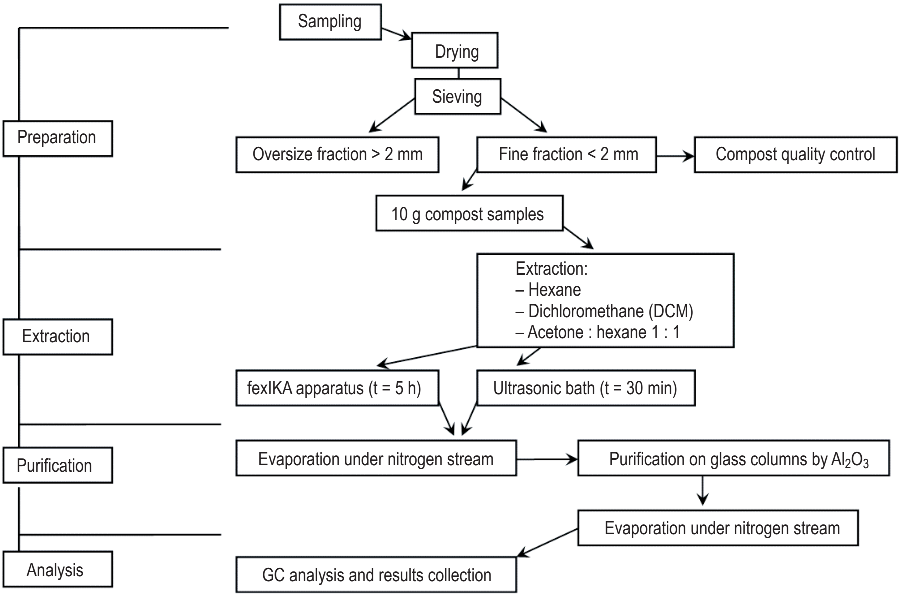

Fig. 1. Experiment scheme

- – 0.5 cm of waterless sodium sulphate,
- – 0.5 g of neutral aluminium oxide dried in 130 °C,
- – 0.5 cm of waterless sodium sulphate.

When the process of filling was finished, dichloromethane was drained and the column was washed three times with 1 cm^3 of hexane, each time. The subsequent stage was to fill the column with hexane and slow drain it to the level of approximately 3 mm over the surface of sodium sulphate and put the sample on the prepared column. The column was washed again four times with 1 cm^3 of hexane and eluate was rejected each time. In order to leach the fraction containing PAHs, 40 % of DCM solution in hexane was used, after this the obtained eluate was inspissated to approximately 300 mm^3 (μl). Prepared in such a way the sample underwent analysis through a gas chromatograph Varian GC 3800 with the usage of ZB-5 column (length – 30 cm).

The procedure of extraction and quantity-quality measurements of PAHs in compost samples was carried out simultaneously in two attempts. Concentration of the analysed compounds were given in mg/kg d.m. With accuracy to the 0.001 mg/kg d.m. and as a percentage contents of particular PAHs with accuracy to the 0.01 %.

Results and discussion

The basic characteristic of compost, which underwent analysis, is presented in Table 1.

Table 1

Main characteristic of compost

Parameter	Unit	Value
Fraction	[mm]	< 2
pH_{H_2O}	—	7.78
Organic matter	[%]	33.8
Organic carbon	[%]	18.5
Humidity	[%]	4.4
Nitrogen	[% N_{Kjeld}]	0.86
Phosphorus	[% P_2O_5]	1.23
Potassium	[% K_2O]	0.65
Glass	[%]	< 0.1

When it comes to the basic characteristic of compost from the municipal waste it was proven that of all organic substances 54.73 % is organic carbon. The paper also examined extraction methods of the polycyclic aromatic hydrocarbons contained in compost from the municipal waste. The following extractants were used: hexane,

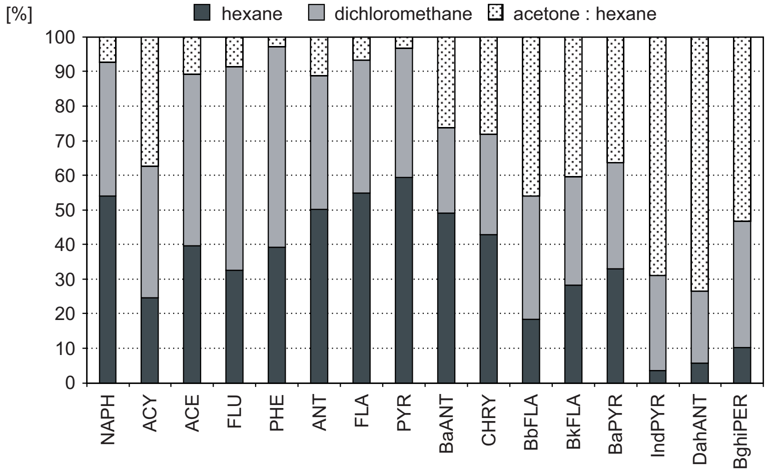

Fig. 2. The percentage participation of Polycyclic Aromatic Hydrocarbons (PAHs) in compost, which underwent extraction process in the ultrasonic bath

dichloromethane as well as acetone and hexane in a ratio of 1:1 by volume. When it comes to the process of separation the particular PAHs were carried out by using ultrasound and the fexIKA device.

The percentage participation of Polycyclic Aromatic Hydrocarbons (PAHs) in compost, which underwent an extraction process in the ultrasonic bath (Fig. 2).

In the compost samples extracted by hexane the definite majority constituted of compounds with three and four benzene rings arranged in a cluster spatial layout in the molecule. Among these the majority were: fluoranthine (20.13 %), pyrene (17.82 %) and chrysene (15.01 %).

A similar situation occurs when dichloromethane is used as an extractant. When extracting PAHs by acetone and hexane in a ratio of 1:1, six-cyclic hydrocarbons are the most easily separated, especially: indeno(1,2,3-c,d)pyrene (22.57 %) and benzo(g,h,i)perylene (16.11 %). Changes in the content of Polycyclic Aromatic Hydrocarbons (PAH) in compost extracted in the fexIKA device (Fig. 3).

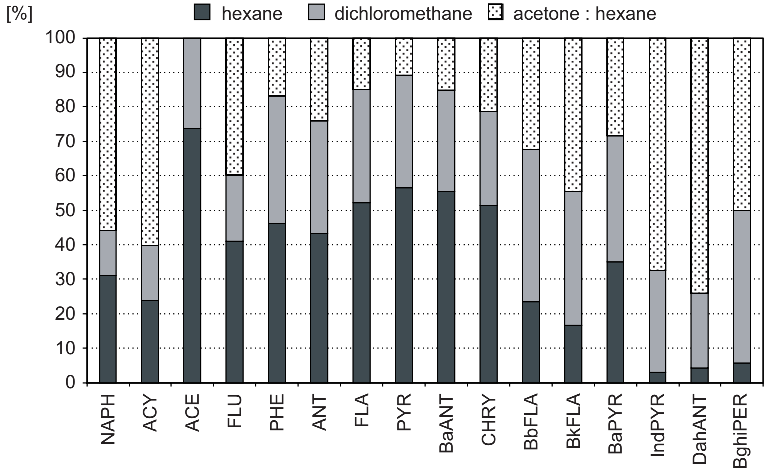

Fig. 3. Changes in the content of Polycyclic Aromatic Hydrocarbons (PAHs) in compost extracted in fexIKA

The biggest group was PAHs with three- and four-cyclic molecules, including cluster spatial layout, extracted by hexane. In this group of compounds the most common were: fluoranthene (19.83 %), pyrene (17.58 %) and chrysene (18.15 %). A similar content of Polycyclic Aromatic Hydrocarbons was noted in compost, which underwent the process of extraction by dichloromethane in comparison with the content of PAHs in compost extracted by hexane. The only exception were the six-cycle compounds, which are ideno(1,2,3)pyrene (11.81 %) and benzo(g,h,i)perylene (11.50 %). Using acetone and hexane in a ratio of 1:1 as an extractant, the best separated were six-cycle compounds, that is indeno(1,2,3)pyrene (26.79 %) and benzo(g,h,i)perylene (13.02 %). The comparison of extraction methods by selected solvents was carried out as well (Fig. 4).

The best solvent used in the extraction process of compost, containing polycyclic aromatic hydrocarbons in water bath was dichloromethane. By this extractant an overall

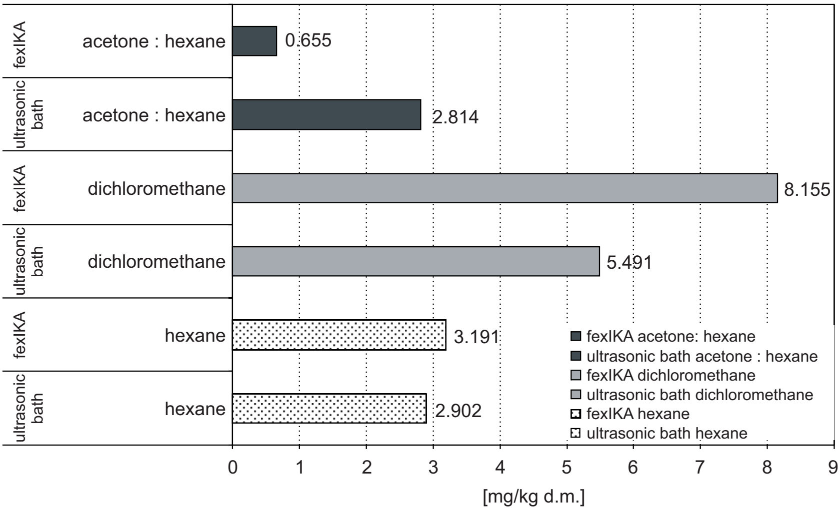

Fig. 4. Comparison of extraction methods using different solvents

PAH content of 5.491 mg/kg d.m. was obtained during the research. When comparing the overall concentration of 16 PAHs in compost which underwent sonication by hexane, the overall concentration of PAHs was 2.814 mg/kg d.m. The total concentration of PAHs in compost that underwent sonication by acetone and hexane in a ratio of 1:1 was 2.902 mg/kg d.m. It was found that these values are very similar [5]. The research shows that when using the fexIKA vario control cycle for the extraction process it is better to use dichloromethane as the extractant. By contrast, the least effective method of extraction was by acetone and hexane in a ratio of 1:1 by volume.

Conclusions

The research has led to the following conclusions:

Applying hexane as an extractant allows a separation of mainly three- and four-cyclic compounds. Six-cycle hydrocarbons are extracted most efficiently by acetone and hexane in a ratio of 1:1. Nonetheless, the best extractant in the process of PAHs extraction, either by ultrasounds or by the fexIKA device, is dichloromethane.

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EFEKTYWNOŚĆ WYBRANYCH METOD EKSTRAKCJI PAHs (WWA) NA PRZYKŁADZIE KOMPOSTU Z ODPADÓW KOMUNALNYCH

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Abstrakt: Techniki ekstrakcyjne odgrywają szczególną rolę na etapie przygotowywania próbek do identyfikacji i wydzielania analitów z próbek środowiskowych. Anality, będące głównie stałymi substancjami organicznymi, z materiałów stałych można wyodrębnić albo za pomocą gazu, albo przy użyciu rozpuszczalnika. W dalszym ciągu, jako ekstrahenty analitów, najbardziej popularnymi i najczęściej stosowanymi są różne rodzaje rozpuszczalników. Sprawność ekstrakcji nie zależy jednakże tylko od rodzaju rozpuszczalnika, ale też od metody ekstrakcji. W literaturze podawane są najróżniejsze metody oznaczania zarówno ilościowego jak i jakościowego trwałych zanieczyszczeń chemicznych, jakimi są m.in. wielopierścieniowe węglowodory aromatyczne. Praca ta miała na celu przetestowanie zarówno różnych rozpuszczalników organicznych, tj. heksanu, dichlorometanu oraz heksanu i acetonu, jak i różnych metod ekstrakcji w procesie izolacji wielopierścieniowych węglowodorów aromatycznych z kompostu pochodzącego z odpadów miejskich.

Słowa kluczowe: ekstrakcja, PAHs, kompost

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COMPUTER SIMULATION OF FLOCCULATION AND CHEMICAL COAGULATION

SYMULACJA KOMPUTEROWA PROCESU FLOKULACJI I KOAGULACJI CHEMICZNEJ

Abstract: In the present study, a computer program was employed to simulate the coagulation of suspended solids. The paper provides a description of the developed simulation program. The reaction order of the coagulation process was determined, and the effect of the initial velocity of sol particles and the size of sol and coagulant particles on the rate of coagulation was investigated. The tested program was found to comply with the classical theories of particle motion and colloidal system destabilization. The rate of the simulated coagulation process satisfied second-order kinetic equations and the Smoluchowski equation. As expected, a simulated increase in the initial velocity of sol particles increased the rate of coagulation. An increase in the sol particle diameter had a more significant effect on the rate of coagulation than an increase in the coagulant particle diameter.

Keywords: coagulation, flocculation, simulation, sol

Although the technologies of chemical and biological-chemical wastewater treatment are constantly being improved, coagulation remains the most popular and widely applied method. The complex coagulation-flocculation process can be classified as orthokinetic or perikinetic. In orthokinetic coagulation, the particles collide due to the effect of external factors. The process may be accelerated by stirring which increases the probability of collisions between single colloidal particles and agglomerates. The final result of orthokinetic coagulation is dependent upon the amount of mechanical energy dispersed per unit volume. An excessive amount of energy prevents colloid flocculation [1], and the force of gravity may inhibit the gelation of suspended solids [2]. In perikinetic coagulation, the particles move by random Brownian motion and collide. Perikinetic coagulation takes place, among others, in pre-sedimentation and

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septic tanks at wastewater treatment plants. Since colloidal particles suspended in wastewater have low kinetic energy, destabilization and colloid precipitation occur at a slow rate.

Due to its complexity, the coagulation process continues to receive the attention of researchers and practitioners, and it is studied from both a fundamental (the mechanism and kinetics of particle flocculation) [3–6] and a utalitarian perspective [7–8]. Coagulation, aggregation, flocculation and sedimentation processes are usually investigated in natural systems, such as wastewater [9, 10], model systems, including silica suspensions [11], as well as computer-simulated systems [12–14]. Computer-assisted simulations offer unlimited experimental options, supporting the description of molecular collision models, the mechanism of latent, slow and rapid coagulation, as well as the conditions and the kinetic parameters of those processes [15–19]. The results of computer-aided simulations support the development of fundamental databases, and the resulting conclusions and suggestions [20] render them an interesting alternative to applied research.

Contemporary research often relies on Monte Carlo simulation methods. This approach is based on the theory of probability and statistical mechanics, and it is widely applied to calculate the fractal dimensions of aggregates, investigate their structure, and to study the mechanism of aggregation, coagulation and flocculation processes [21–25].

In the present study, a computer program (ZB2) was employed to simulate the coagulation of suspended solids. The kinetics of chemical coagulation and the reaction order of the coagulation process were determined. The effect of the initial velocity of sol particles and the size of sol and coagulant particles on the rate of coagulation was also investigated.

Methods

The ZB2 program was written in Pascal. The program simulates the coagulation, flocculation and sedimentation of spherical sol particles with the use of spherical coagulant particles [26]. The applied simulation model is a stochastic and a dynamic model based on random variables, and its state changes over simulation time. The simulation program features a module solving the equation of motion of a given number of points (particles) in a closed vessel. The initial particle location values are randomly generated in line with a homogenous system in the vessel area. The direction of particle movement and their initial location are randomly drawn using the RANDOM command. The angle at which a particle hits the wall is always equal to the angle of incidence. The velocity of a cluster that hits the bottom decreases by 30 %. The following input data were adopted:

– A – number of coagulant particles: A = const = 100;

– B – number of sol particles: B = const = 1000;

– C – initial velocity of a coagulant particle: C = 5, 10, 15, 20, 25, 30, 35 and 40;

– D – initial velocity of a sol particle: $D = 2C$, ie, 10, 20, 30, 40, 50, 60, 70, 80 and $D = 5C$, ie, 25, 50, 75, 100, 125, 150, 175 and 200;

– E – “coagulation threshold”, ie a parameter indicating the number of sol particles which initiate the sedimentation of a cluster/floc containing one coagulant particle: $E = \text{const} = 10$;

– F – “sedimentation coefficient”: $F = \text{const} = 0.2$;

– G – simulated average diameter of a coagulant particle. Changes in G are not displayed on the screen, but they become visible as the distance between the particles in the formed floc increases. The smaller the diameter of the coagulant particle, the lower the probability of collision with a sol particle: $G = 1, 2, 3$ and 4;

– H – simulated average diameter of a sol particle: $H = 1, 2, 3$ and 4;

– I – simulated ratio of the mass of a coagulant particle to the mass of a sol particle determined by the values of G and H.

The program was equipped with the S = stop function (timer) measuring the time of the simulated process as well as a meter counting the number of “coagulated” particles in the sediment because the program counts particles with the velocity of $C = 0$.

All tests were performed in seven replications. Two maximum values and two minimum values were discarded to compute the arithmetic mean based on three measurements.

Results and discussion

In line with the adopted methodology, the number of deposited coagulant particles A and the number of sol particles B (waste) was counted every time after stimulated time t [simulated second]. Reaction order was determined graphically through the conversion (linearization) of generally applied kinetic equations of first-order (a) and second-order (b) reactions, respectively:

a) $t = f\,\{2{,}303\ \ln\,[1100/(A + B)]\}$,

b) $t = f\,[1/(A + B) - 1/1100]$.

The number 1100 appearing in equations a) and b) is the initial, ie at $t = 0$, total number of coagulant particles A and sol particles B in the system:

$$1100 = A(100) + B(1000)$$

Tables 1 and 2 demonstrate the effect of changes in the initial velocity of each coagulant particle C, accompanied by the proportional values of the initial velocity of each sol particle D, on the rate of the coagulation process.

$$D = 2 \cdot C \text{ – Table 1, } D = 5 \cdot C \text{ – Table 2}$$

In practice, changes in the initial velocity of any particle result from alterations in temperature or stirring intensity, since both parameters always lead to changes in the studied object’s kinetic energy.

Table 1

The values of first-order and second-order reaction rate constants and the values of determination coefficient R^2 for *C* and *D* pairs from 5 and 10 to 40 and 80

C, *D*, *E*, *G*, *H*, *I*	R^2 for I order	$k_I \cdot 10^{-2}$	R^2 for II order	$k_{II} \cdot 10^{-5}$
5; 10; 10; 2; 2; 1	0.899	1.58	0.971	0.916
10; 20; 10; 2; 2; 1	0.941	1.98	0.991	1.16
15; 30; 10; 2; 2; 1	0.921	2.13	0.980	1.24
20; 40; 10; 2; 2; 1	0.946	2.29	0.988	1.34
25; 50; 10; 2; 2; 1	0.970	2.94	0.981	1.73
30; 60; 10; 2; 2; 1	0.978	3.51	0.984	2.07
35; 70; 10; 2; 2; 1	0.957	3.39	0.988	1.99
40; 80; 10; 2; 2; 1	0.968	3.89	0.981	2.29

Table 1 presents selected k_I, k_{II} and R^2 values for *C* and *D* pairs from 5 and 10 to 40 and 80. As anticipated, an increase in the particles' initial velocity was accompanied by an increase in the rate of the investigated coagulation process, expressed by the rate constants of both first-order (k_I) and second-order reactions (k_{II}). The values of the corresponding coefficients of determination R^2 for the second-order model were always higher than for the first-order model. The use of a second-order model in the examined simulation produced an average $R^2 = 0.983$, which was higher than the average $R^2 = 0.948$ reported in the first-order model.

Table 2

The values of first-order and second-order reaction rate constants and the values of determination coefficient R^2 for *C* and *D* pairs from 5 and 25 to 40 and 200

C, *D*, *E*, *G*, *H*, *I*	R^2 for I order	$k_I \cdot 10^{-2}$	R^2 for II order	$k_{II} \cdot 10^{-5}$
5; 25; 10; 2; 2; 1	0.934	1.86	0.985	1.08
10; 50; 10; 2; 2; 1	0.951	3.17	0.987	1.85
15; 75; 10; 2; 2; 1	0.976	3.72	0.950	2.21
20; 100; 10; 2; 2; 1	0.938	4.66	0.977	2.73
25; 125; 10; 2; 2; 1	0.913	5.58	0.965	3.25
30; 150; 10; 2; 2; 1	0.886	6.98	0.935	4.08
35; 175; 10; 2; 2; 1	0.923	7.61	0.949	4.47
40; 200; 10; 2; 2; 1	0.927	8.16	0.929	4.81

Table 2 illustrates selected k_I, k_{II} and R^2 values for *C* and *D* pairs from 5 and 25 to 40 and 200. Similarly to the data shown in Table 1, the values of the corresponding coefficients of determination R^2 for the second-order model were higher in comparison with the first-order model. The use of a second-order model in the studied process produced an average $R^2 = 0.960$, which was also higher than the average $R^2 = 0.932$ for the first-order model. The results indicate that the coagulation process was a second-order reaction. This suggests that the applied ZB2 system is fully consistent with Smoluchowski's theory of coagulation kinetics [27], and the coagulated system has the features of a monodispersive sol. In view of the observed results, *G* = *H*, therefore, the average diameter of a coagulant particle was identical to the diameter of a sol particle.

The correlation between the coagulation rate (k_{II}) and the initial velocity of sol particles *D* is illustrated in Figs. 1a and 1b. It was assumed that the kinetic energy (initial velocity) of a single coagulant particle should be at least twice lower than the kinetic energy of a single sol particle because the aim of every coagulant particle is to "collect" 10 sol particles, and not the other way around. For this reason, in Fig. 1a, the initial velocity of coagulant particles, determined in the range of *D* = 10–80, was set at half the initial velocity of sol particles (*C* = 5–40), whereas the data shown in Fig. 1b, covering a more extensive range of *D* = 25–200, always required *D* = 5*C* to support the examination of a range identical to that in Fig. 1a (*C* = 5–40). Therefore, Figs. 1a and 1b demonstrate the effect of the initial velocity of two types of sol particles on the coagulation rate with the use of an identical coagulant. The resulting database effectively illustrates the simulation of the coagulation of different sols using the same coagulant. The simulated variation in the initial velocity of a sol particle, where particle diameter (*G* = *H* = 2) and the density of sol and coagulant particles (*I* = 1) remained constant, implies that the simulated coagulation took place after the preliminary heating of sol from the temperature indicated in Fig. 1a to that in Fig. 1b, or after the preliminary, intense stirring of sol particles in Fig. 1a to achieve the velocity shown in Fig. 1b. Coagulant particles were introduced to the system after the heating or stirring of the "waste", and they were subjected to the analyses shown in Fig. 1b.

In the range of *D* = 25–80, shared by both figure drawings, preliminary heating (or stirring) had an insignificant effect on the coagulation rate (k_{II}), although every simulated increment in sol particles' initial velocity increased the coagulation rate within the entire measurement range. According to the data in Fig. 1b, the maximum coagulation rate is $k_{II} = 4.81 \cdot 10^{-5}$, while in Fig. 1a, the maximum coagulation rate is $k_{II} = 2.29 \cdot 10^{-5}$ at the same initial velocity of coagulant particles. The above implies that *D* = 200/*D* = 80, therefore, a 2.5-fold increase in sol particles' initial velocity produces only 4.81/2.29 = 2.1-fold increase in the studied sol's coagulation rate.

According to Fig. 1a, the value of k_{II} calculated from a regression equation reached $k_{II}(10) = 0.8981 \cdot 10^{-5}$ for *D* = 10 and $k_{II}(80) = 2.2841 \cdot 10^{-5}$ for *D* = 80. This

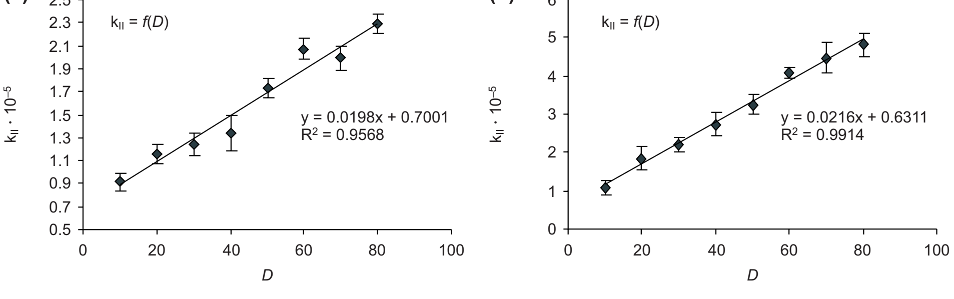

Fig. 1. The correlation between the coagulation rate and the initial velocity of sol particles (*D*) at a two-fold lower velocity of coagulant particles *C*, *D* = 2*C* (a), at a five-fold lower velocity of coagulant particles *C*, *D* = 5*C* (b)

demonstrates than an 8-fold increase in sol particles' initial velocity resulted in 2.2841/0.8981 = a mere 2.5-fold increase in the coagulation rate. Within the range shown in Fig. 1b, the value of k_{II} calculated from a regression equation reached $k_{II}(25) = 1.1711 \cdot 10^{-5}$ and $k_{II}(200) = 4.9511 \cdot 10^{-5}$. As above, an 8-fold increase in sol particles' initial velocity produced only 4.9511/1.1711 = 4.3-fold increase in the coagulation rate. The observed results support the following conclusion: "$D = 5C/D =$ $= 2C$ = a 2.5-fold increase in sol particles' initial velocity produces only 4.3/2.5 = an estimated 1.7-fold increase in the rate of the simulated coagulation process". The above conclusion has a number of practical implications that can be laconically expressed as follows: before coagulation, ie before introducing the coagulant to the waste, the waste should not be **excessively** heated or stirred because the cost of those operations will not be compensated by the rate or the effectiveness of the waste coagulation (purification) process.

The effect of sol particles' diameter (H from 1 to 4) on the coagulation rate (k_{II}) at four values of G, ie G = 1, 2, 3 and 4, is presented in Fig. 2. The ratio of a coagulant particle's mass to a sol particle's mass I was investigated on the assumption that coagulant and sol particles have identical density, therefore it was calculated each time as G^3/H^3. The resulting graph comprises four +/– parallel, increasing linear functions, which is consistent with expectations because an increase in particle diameter maximizes the probability of an active collision. According to Arrhenius [28], the rate of any chemical reaction, including coagulation, is directly proportional to the number of active collisions in a unit of time. The simulated reaction (coagulation) shows that within the analyzed range, an increment in the value of H by one unit increases the reaction rate (k_{II}) by approximately $0.6 \cdot 10^{-5}$ (refer to the slopes of the respective straight lines in Fig. 2). The parallel lines in Fig. 2 remain separated by a fixed distance of approximately $0.3 \cdot 10^{-5}$ (k_{II}). Therefore, it can be postulated that an increment in the value of G by one unit increases the reaction rate by 20 %. In the examined combinations of G and H, the coagulation rate at $D = 2C$ was more affected by an

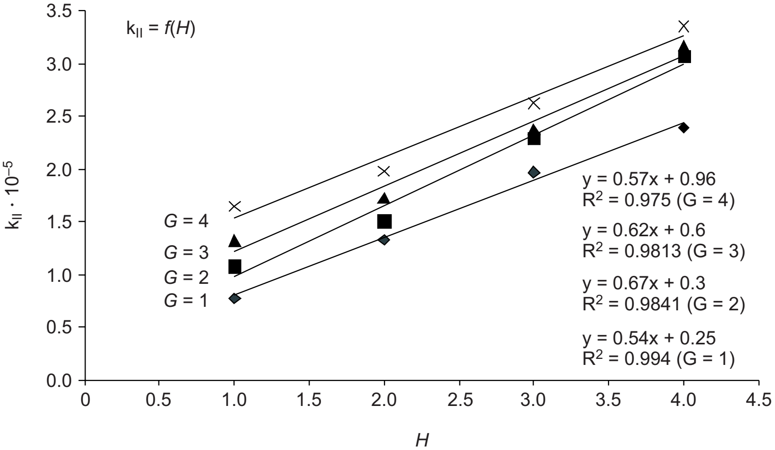

Fig. 2. The correlation between the coagulation rate and particle diameter at $D = 2C$

increase in the diameter of a sol particle than a coagulant particle. This fact is a logical consequence of the imposed proportions between the number of coagulant particles and sol particles at $A/B = 100/1000 = 0.1$. An increase in the diameter of sol particles marked by a 10-fold excess in the simulated coagulation system is more likely to increase the probability of an active collision with a coagulant particle than an increase in the diameter of coagulant particles remaining in a 10-fold minority.

Figure 3 illustrates the effect of sol particles' diameter (H from 1 to 4) on the coagulation rate (k_{II}) at two values of G, ie $G = 1$ and $G = 3$. Similarly to Fig. 2, the ratio of a coagulant particle's mass to a sol particle's mass I was investigated on the assumption that coagulant and sol particles have identical density, therefore, it was calculated as G^3/H^3. As anticipated, the resulting graph comprises two parallel, increasing linear functions because an increase in particle diameter maximizes the probability of an active collision. The course of the simulated reaction (coagulation) indicates that within the studied range, an increment in the value of H by one unit increased the reaction rate (k_{II}) by approximately $0.62 \cdot 10^{-5}$ – as calculated from the regression equation for $G = 3$. This value closely approximates the results shown in Fig. 2. The parallel lines in Fig. 3 remain separated by a fixed distance of approximately $0.42 \cdot 10^{-5}$, which is nearly 1.5-fold greater than the distance indicated in Fig. 2. The absolute reaction rate values were higher by around 30–40 %, which does not correspond to the higher D values, from $D = 2C$ (Fig. 2) to $D = 5C$ (Fig. 3).

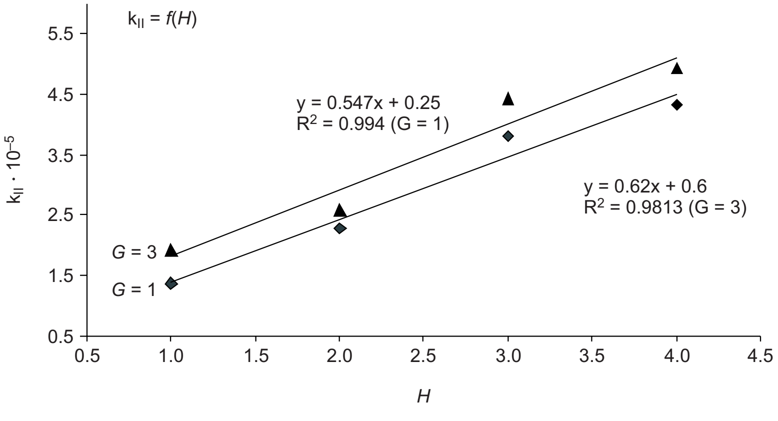

Fig. 3. The correlation between the coagulation rate and particle diameter at $D = 5C$

According to the kinetic theories postulated by Smoluchowski, Muller and others [27–29], the radius of a particle involved in the coagulation process affects the rate and the effectiveness of coagulation. Based on the work of Arrhenius [28] investigating the frequency of active collisions = reaction rate, eg k_{II}, the number of active collisions for second-order reactions is determined by particle radii as follows:

$$k_{II} \ \alpha \ (G + H)^2$$

The above implies that the reaction rate is directly proportional to the square of total radii (diameters) of reagent particles. The results of this study do not "fit" the above dependency. The discrepancies in the results of experiments investigating the kinetics of standard chemical reactions and laboratory experiments analyzing the coagulation kinetics of hydrosols have led to the creation and the popularization of the above coagulation kinetics theories (including Smoluchowski's theory). In different mathematical models, eg expressing the probability P that one particle will collide with another particle:

$$P = 4 \cdot \pi \cdot A \cdot D_r$$

where: A – radius of particle attraction, and D_r – coefficient of diffusion, the value of diffusion coefficient D_r is determined by the dimensions of coagulating particles.

The Smoluchowski formula and its modified version:

$$P = 4 \cdot \pi \cdot A \cdot D_r \cdot \xi$$

where ξ – fraction of effective collisions determined by coagulant concentrations, are used to determine the probability of particle collisions in both slow and rapid perikinetic coagulation of monodispersive sols. The methodological constraints of the discussed simulation prevented rapid or slow orthokinetic coagulation in the studied environment.

Summary and conclusions

This study investigated the effect of changes in the initial velocity of every coagulant particle C, combined with the proportional value of initial velocity of each sol particle D, because in practice, changes in the initial velocity of any particle result from alterations in temperature or stirring intensity, and both parameters always lead to changes in the studied object's kinetic energy.

The values of first-order and second-order reaction rate constants, k_I and k_{II}, and the respective values of determination coefficients R^2 indicate that the values of determination coefficients R^2 for the second-order reaction model were always higher than those noted in the first-order reaction model. The use of a second-order reaction model in the analyzed simulation was therefore correct from both the theoretical and the practical perspective. The ZB2 model complies with the theory of coagulation kinetics proposed by Smoluchowski, and the studied coagulation system has the features of a monodispersive sol.

The simulated variations in the initial velocity of a sol particle, where particle diameter ($G = H = 2$), sol and coagulant density remained constant ($I = 1$), show that the simulated process takes place after the preliminary heating or intense stirring of sol. Preliminary heating (or stirring) had an insignificant effect on the coagulation rate, although the anticipated stimulated increment in sol particles' initial velocity increased the coagulation rate within the entire measurement range. A 2.5-fold increase in sol particles' initial velocity resulted in only 4.81/2.29 = 2.1-fold increase in the coagulation rate.

The discussed experiment also investigated the effect of sol particles' diameter on the coagulation rate. The authors concluded that the rate of any chemical reaction, including coagulation, is directly proportional to the number of active events. In the simulated process (coagulation), an increase in sol particles' diameter by a simulated unit accelerated the process by only 20 %. An increase in the diameter of sol particles was more likely to increase the rate of coagulation than an increase in the diameter of coagulant particles. The above was a logical consequence of the imposed proportions between the number of coagulant particles and sol particles. The increase in the coagulation rate resulting from a simulated increase in the size of sol particles proved to be smaller than anticipated.

The results of this study have prompted the authors to formulate the following conclusions:

1. The ZB2 computer application correctly simulates the process of chemical coagulation of hydrosols.
2. The simulated chemical coagulation proceeds in line with the kinetic equation for a second-order reaction.
3. The simulated sol had the features of a monodispersive sol in the analyzed range of parameters.
4. The variations in the initial velocity of sol particles are induced by the heating or preliminary stirring of sol (eg waste) before coagulation.
5. Excessive heating or stirring of sol (waste) before coagulation is not justified in view of the resulting rate and effectiveness of the coagulation process.
6. The rate of coagulation is insignificantly affected by particle size. The size of sol particles has a greater effect on the coagulation rate than the size of coagulant particles.

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SYMULACJA KOMPUTEROWA PROCESU FLOKULACJI I KOAGULACJI CHEMICZNEJ

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Abstrakt: Opisano wyniki badań przeprowadzonych przy zastosowaniu komputerowego programu „ZB2” symulującego koagulację zawiesiny zawierającej kuliste cząstki zolu i kuliste cząstki koagulantu. Przedstawiono charakterystykę opracowanego programu, a następnie opisano wyniki badań wpływu prędkości początkowej zolu oraz rozmiar cząstki zolu i koagulantu na szybkość procesu koagulacji. Wykazano, iż program „ZB2” pozostaje w zgodności z klasycznymi teoriami ruchu cząstek i destabilizacji układów koloidalnych. Szybkość symulowanego procesu koagulacji, w zakresie opisanym w niniejszej pracy, spełniała równanie kinetyczne II rzędu, a także równanie Smoluchowskiego. Symulowany wzrost prędkości początkowej cząstek zolu zgodnie z oczekiwaniem powodował wzrost szybkości koagulacji. Okazało się także, że większy wpływ na szybkość koagulacji miało zwiększenie średnicy cząstki zolu, aniżeli zwiększenie średnicy cząstki koagulantu.

Słowa kluczowe: koagulacja, flokulacja, symulacja, zol

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REACH REGULATION AS A FORM OF PROTECTION OF THE ENVIRONMENT. REACH PRE-REGISTRATION AND REGISTRATION – SUMMARY AND STATISTICS

ROZPORZĄDZENIE REACH JAKO FORMA OCHRONY ŚRODOWISKA. REJESTRACJA WSTĘPNA I WŁAŚCIWA – PODSUMOWANIE I STATYSTYKI

Abstrakt: The REACH Regulation is a Directive of the European Parliament and Council concerning the safe use of chemicals through their registration, authorisation and evaluation. An important change from the previous EU chemicals legislation is that, under REACH, responsibility for the management of the risks lies with the company that manufactures, imports, places on the market or uses a substance in the context of its professional activities. The safe use of chemicals is the core objective of REACH. Industry is responsible for establishing the safety of chemicals. Companies must demonstrate that they use their substances safely and provide accurate data in their registration dossiers. The results of these tests must be submitted to the Chemical Agency in Helsinki. Pre-registration, which took place between 1st June and 1st December 2008, required manufacturers and importers to provide a limited set of information on the phase-in substances they intend to register (no data, no market), in order to be entitled to take advantage of the transitional provisions for registration. Pre-registration is the starting point for the formation of Substance Information Exchange Fora (SIEF), where manufacturers and importers who pre-register can exchange information and jointly prepare the information to be submitted for registration. The next stage (which is anticipated to last for 10.5 years) is the registration, which is taking place now. The registration requires performing many specific tests of produced or imported substances, depending on their tonnage and influence on human health and the environment. The reports published by the Agency allow tracking the statistics concerning the course of the registration and the share of individual countries in the process. At this stage of implementing the Regulation, the course of the pre-registration can be summed up and a general assessment of the course of the registration can be performed. After completing the registration, there will be started the process of verifying the data presented by the registering entities, which can last for a long time. The new system results in the necessity of

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bearing the administrative costs and the costs of preparing the data required for European registration, but it also offers an opportunity of learning about the influence of chemicals on the environment and on health of humans and animals. This knowledge will surely allow avoiding many threats connected with the use of unknown and untested chemicals.

Keywords: REACH, pre-registration, registration, statistics

The REACH Regulation: R – Registration, E – Evaluation, A – Authorisation of CH – CHemicals.

The main requirement of the Regulation addressed to the industry is the necessity of registering chemicals in accordance with its contents and the timeline imposed by it (Fig. 1).

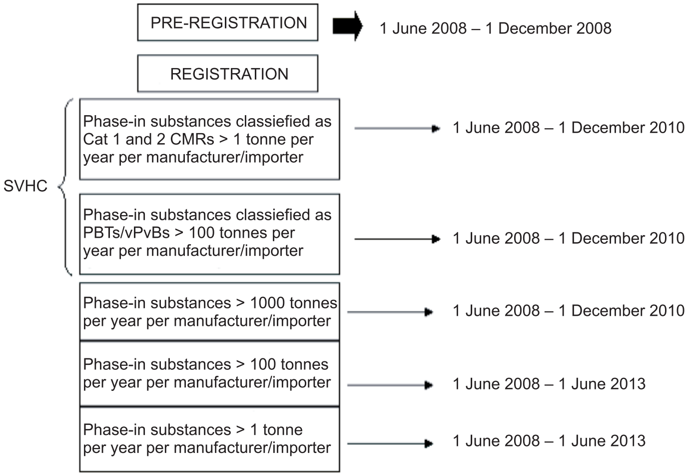

Fig. 1. Registration time limits (SVHC – Substances of Very High Concern; CMRs – Carcinogenic, Mutagenic or toxic Reproduction.; PBTs – Persistent Bioaccumulative Toxics; vPvBs – substances which are very Persistent and very Bioaccumulative)

In compliance with the provision II of the Regulation (EC) No. 1907/2006, known as REACH Regulation, each substance, on their own, contained in a preparation or a product imported into the territory of EU in an amount higher than 1 Mg a year must be registered in accordance with the provisions of this Regulation [1]. Substances, on their own means a chemical element and its compounds in the natural state or obtained by any manufacturing process, including any additive necessary to preserve its stability and any impurity deriving from the process used, but excluding any solvent which may be separated without affecting the stability of the substance or changing its composition. Preparation means a mixture or solution composed of two or more substances and article means an object which during production is given a special shape, surface or design which determines its function to a greater degree than does its chemical composition [1].

The period for implementing the REACH system, in particular, preparing and performing the registration of chemicals produced in or imported into the territory of the

European Union was foreseen for 11 years. However, this is not the total time required for implementing this system, because after completing the registration, there will begin the process of verifying the data presented by the registering entities, which can last for a long time.

An indirect requirement of the Regulation is the necessity of performing many specialist tests, the scope of which would depend on the tonnage and type of a substance as well as on its impact on the health of people and animals and on the environment.

The work on the Draft REACH Regulation

The problem of possible negative influence of chemicals attracted attention before 1981, when it was found that over 100 000 substances, which had not been earlier subject to any legal obligation of testing them in respect of their possible harmful effects on human health and negative influence on the environment, had been placed on the market of the European Economic Community. In that year, EEC introduced the requirements about testing chemical substances as a response to the increased incidence of cancer and other diseases caused by these substances. In this way, a broad review and tests of the chemicals being marketed were started. In 1998, the European Council for the Environmental Issues decided to revise the community law concerning chemicals and to propose a new system, which would allow evaluating the chemical substances being marketed in a profound and harmonized manner [2]. On 18 December 2006, EU Council adopted, without any discussion, the REACH package in the wording that was approved also by the European Parliament, and on 30 December 2006 this package was promulgated in the Official Journal of the European Union. As of 1st June 2008, European manufacturers and importers of chemicals were obliged to report, within six months, the fact of producing or importing any substances being marketed in the area of EC countries in the quantities over 1 Mg a year [3].

Pre-registration and registration

Pre-registration, which took place between 1st June and 1st December 2008, required manufacturer and importer to provide a limited set of information on the phase-in substances they intend to register (no data, no market), in order to be entitled to take advantage of the transitional provisions for registration [5].

When drawing up the REACH Regulation, the Commission estimated that over 130000 pre-registrations would be received from industry, for more than 70000 chemical substances and intermediates. By the end of the pre-registration period, ECHA had received 20 times more pre-registrations than expected (Fig. 2).

Many of these pre-registrations were – for a number of reasons – submitted by companies that will not submit a registration later in the process. However, the high volume of pre-registrations created a significant additional workload for ECHA staff and resulted in a temporary overload of the IT system, which led to an intense

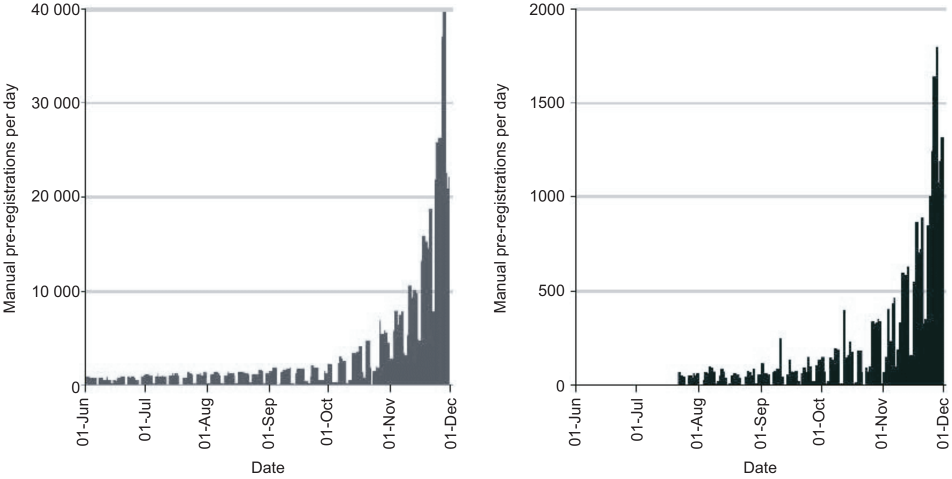

Fig. 2. Number of pre-registrations per day from 1st June to 1st December 2008 [6]

period of communication with stakeholders regarding the progress on the system usability.

Breakdown of pre-registrations and legal entities per country is presented in the figure below (Fig. 3).

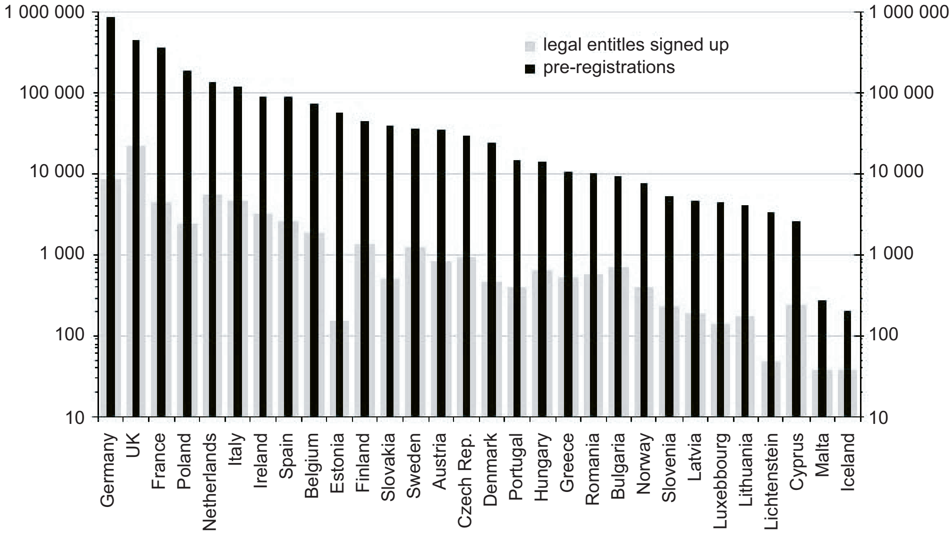

Fig. 3. Breakdown of pre-registrations and legal entities per country [6]

Registration began on 1st June 2008. By 31st December 2008, 1538 dossier submissions (810 inquiries, 487 PPORD notifications (*Product and Process Oriented*

Research and Development) and 241 registrations covering 28 phase-in substances) had been manually handled and processed within the deadlines set by the legal text. Approximately 70 % of dossiers passed the initial checking procedure (which included a virus check) and were then subject to a technical completeness check. The most common causes for not passing the check included inconsistencies in identification of the dossier, substance or company, or basic errors such as failure to include the requested submission form. When a dossier failed the initial technical completeness check, ECHA provided the company responsible for the dossier with a description of the information needed to allow successful re-submission. Duly, many of the submissions, in the above table, concern a second submission of the same dossier.

Table 1

Data submission from 1st June 2008 until 31st December 2008 [6]

Dossier type	Submitted	Accepted for processing	Technical completeness check passed	Complete
Inquiry	810	619	N/A	243
Registrates Intermediates on-site	40	24	12	12
Registrates Intermediates transported	107	70	50	46
Regular Registration dossiers	94	36	10	10
PPORD notifications	487	335	234	228
Total	1538	1084	306	539

The breakdown of registrations by individual countries in 2009 is presented in the figure below. It takes into account the number of registration forms submitted at the Agency in the periods to May, to August, to October and to December.

The basic institution involved in the implementation of the REACH regulation is the European Chemicals Agency (ECHA), established on 1st June 2007, having its office in Helsinki. ECHA's mission is to manage all REACH and CLP tasks by carrying out or coordinating the necessary activities, in order to ensure a consistent implementation at Community level and to provide Member States and the European institutions with the best possible scientific advice on questions related to the safety and the socio-economic aspects of the use of chemicals. This is achieved by ensuring a credible decision-making process, using the best possible scientific, technical and regulatory capacities and by working independently in an efficient, transparent and consistent manner [6]. The Agency, located in Helsinki, Finland will manage the registration, evaluation, authorisation and restriction processes for chemical substances to ensure consistency across the European Union. These REACH processes are designed to provide additional information on chemicals, to ensure their safe use, and to ensure competitiveness of the European industry. In its decision-making the Agency will take the best available scientific and technical data and socio-economic information into account. It will also provide information on chemicals and technical and scientific advice. By assessing and approving testing proposals, the Agency will minimize animal testing [4].

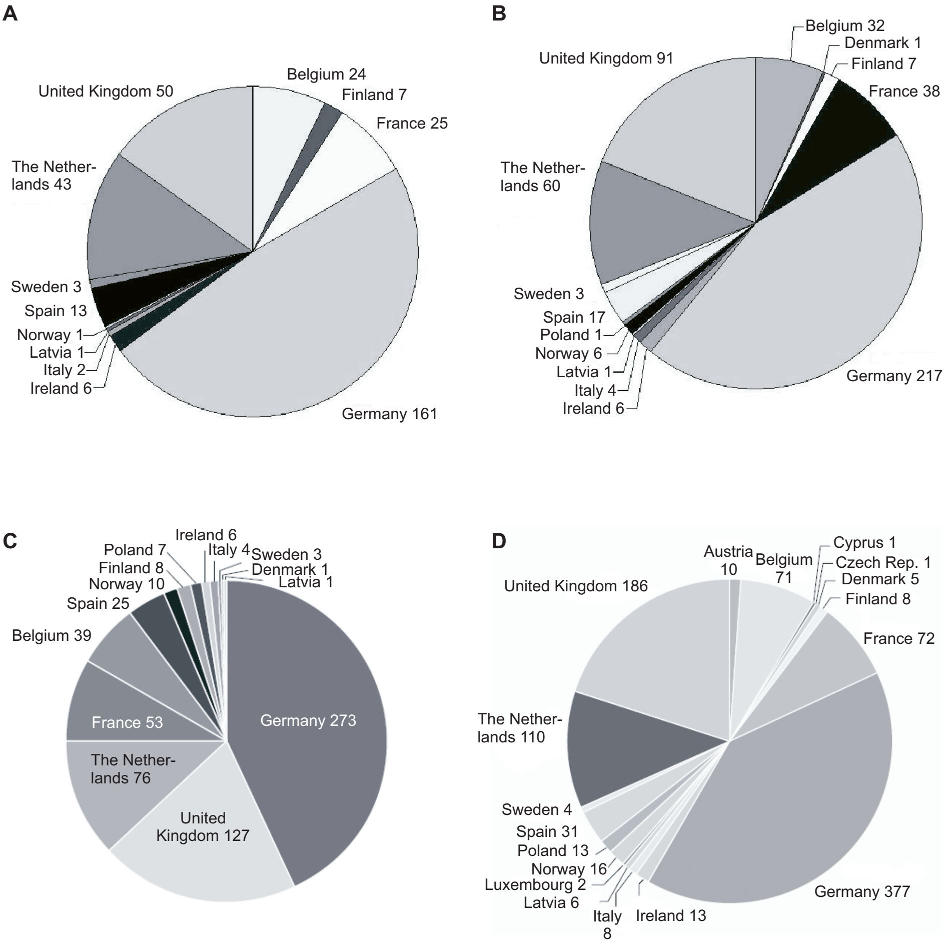

Fig. 4. Submitted registration dossiers by country in 2009 by 3 May (A) – total 336, 4 August (B) – total 484, 5 October (C) – total 633, 11 December (D) – total 939 [7]

Conclusions

One of the aims of the REACH Regulation is to generate information on chemical substances in order that they can be adequately controlled during their manufacture and use. The main mechanisms established in REACH to meet this aim are the registration and pre-registration processes. These processes depend strongly on the scientific IT-tools available to the agency. The tools were developed externally, and were initially the responsibility of the European Commission prior to handover to ECHA [6].

During the six months of the pre-registration period, more than 65000 companies signed up to REACH-IT, submitting more than 2750000 pre-registrations, which covered nearly 150000 different substances. Almost half of the pre-registrations were submitted during the last two weeks of the pre-registration period.

Other notable statistics are that:

– 82 % of companies indicated that they are SMEs (*Small and Medium Sized Enterprises*);

– 25000 companies indicated their intention to register before the first deadline of 30 November 2010, which covers approximately 50000 different substances;

– 18 % of substances were pre-registered without indicating an EC number.

These include mainly:

– substances that do not have an EC number, substances presumably manufactured in the Community but not placed on the market by the manufacturer or importer, and which have phase-in status according to Article 3 [20] (b) (so-called "intermediates");

– substances that have an EC number, which was not used by the potential registrant. These will be identified by ECHA;

– Almost half of the REACH-IT sign ups and pre-registrations were from companies in Germany and the United Kingdom. Other countries with more than 100000 pre-registrations were France, Poland, the Netherlands and Italy [6].

The REACH Regulation is the largest legislative project adopted by the European Union in recent years and the most ambitious chemicals legislation in the world. It aims to address a number of serious shortcomings of the former EU chemicals legislation, in particular the lack of information on risks to human health and the environment for the majority of chemical substances on the EU market and the slowness of the system for dealing with substances identified as hazardous. Chemicals bring real benefits to our everyday life. Some chemicals can, however, also cause serious damage to human health and/or the environment. REACH will make those who place chemicals on the market responsible for understanding the potential adverse effects and managing the risks associated with the use of dangerous chemicals. REACH also aims to enhance the competitiveness of the EU chemicals industry by creating incentives for innovation and by removing distortions of the internal market inherent in the formerly fragmented legislative regime. It was clear from the beginning that implementation of REACH would be a challenging undertaking; not only for the companies concerned but also for ECHA, which is the heart of the new system. The task of breathing real life into REACH operations will very much depend on the quality and effectiveness of the Agency's work, as regards both its own operating procedures, IT systems and the advice and assistance it provides to companies and to Member States [5].

The new system results in the necessity of bearing the administrative costs and the costs of preparing the data required for European registration, but it also offers an opportunity of learning about the influence of chemicals on the environment and on health of humans and animals. This knowledge will surely allow avoiding many threats connected with the use of unknown and untested chemicals.

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[6] European Chemicals Agency, General report 2008. The year of pre-registration, Finland, Helsinki, 24 April 2009; 6-8.
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ROZPORZĄDZENIE REACH JAKO FORMA OCHRONY ŚRODOWISKA. REJESTRACJA WSTĘPNA I WŁAŚCIWA – PODSUMOWANIE I STATYSTYKI

Instytut Technologii Nieorganicznej i Nawozów Mineralnych
Politechnika Wrocławska

Abstrakt: Rozporządzenie REACH jest Dyrektywą Parlamentu Europejskiego i Rady dotyczącą bezpiecznego stosowania chemikaliów, poprzez ich rejestrację, autoryzację i ocenę. Dużą zmianą w stosunku do poprzedniego ustawodawstwa UE w zakresie chemikaliów jest to, że w systemie REACH odpowiedzialność za zarządzanie ryzykiem spoczywa na przedsiębiorstwie, które wytwarza, importuje, wprowadza do obrotu lub stosuje substancję w ramach swojej działalności zawodowej. Bezpieczne stosowanie chemikaliów jest głównym celem systemu REACH. Przemysł odpowiada za ustanowienie substancji chemicznych bezpiecznymi. Przedsiębiorstwa muszą wykazać brak zagrożenia podczas wykorzystywania ich substancji i podać dokładne dane w dokumentacji rejestracyjnej. Badania te muszą zostać przedłożone w Agencji Chemicznej w Helsinkach. Rejestracja wstępna, która trwała od 1 czerwca do 1 grudnia 2008 r., wymagała od producentów i importerów przedłożenia ograniczonego zestawu informacji o substancjach wprowadzonych, które zamierzają zarejestrować (brak danych, brak obrotu), aby nabyć prawo do skorzystania z przepisów przejściowych. Rejestracja wstępna to punkt wyjściowy do tworzenia forów wymiany informacji o substancjach (SIEF), na których producenci i importerzy dokonujący wstępnej rejestracji mogą wymieniać informacje oraz wspólnie przygotowywać je do przedłożenia na potrzeby rejestracji. Kolejnym etapem (przewidzianym na 10,5 roku) jest trwająca obecnie rejestracja właściwa. Rejestracja ta wymaga przeprowadzenia szeregu specyficznych i uzależnionych od tonażu, a także wpływu na zdrowie ludzkie i środowisko badań produkowanych bądź importowanych substancji. Publikowane przez Agencję raporty umożliwiają śledzenie statystyk przebiegu rejestracji jak również udziału w procesie poszczególnych krajów. Na tym etapie wdrażania rozporządzenia można podsumować przebieg rejestracji wstępnej, jak również w okresie do 2010 roku, dokonać poglądowej oceny przebiegu rejestracji właściwej, po zakończeniu której rozpocznie się, mogący trwać długi czas, proces weryfikacji danych przedstawionych przez rejestrujących. Nowy system powoduje konieczność poniesienia kosztów administracyjnych i kosztów przygotowania danych koniecznych do europejskiej rejestracji, ale daje także szansę na poznanie wpływu chemikaliów na środowisko oraz zdrowie ludzi i zwierząt. Wiedza ta z pewnością pozwoli uniknąć wielu zagrożeń związanych ze stosowaniem nieznanych i niezbadanych substancji chemicznych.

Słowa kluczowe: REACH, rejestracja wstępna, rejestracja właściwa, statystyki

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INDEX OF LATIN, POLISH AND ENGLISH SPECIES NAMES OF MICROORGANISMS, PLANTS AND ANIMALS AND THEIR ANATOMICAL PARTS

WYKAZ ŁACIŃSKICH, POLSKICH I ANGIELSKICH NAZW MIKROORGANIZMÓW, ROŚLIN I ZWIERZĄT I ICH CZĘŚCI ANATOMICZNYCH

Meaning of the digits in the index entries – (no. of issue) first page, *no. of the article* (in the volume contents).

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Varia

INNOWACYJNA
GOSPODARKA
NARODOWA STRATEGIA SPÓJNOŚCI

UNIA EUROPEJSKA
EUROPEJSKI FUNDUSZ
ROZWOJU REGIONALNEGO

INFORMACJA O PROJEKCIE „WYKORZYSTANIE KAPUSTY BIAŁEJ NA POTRZEBY FITOREMEDIACJI I BIOFUMIGACJI GLEBY (AGROBIOKAP)”

Projekt nr UDA-POIG.01.03.01-00-138/09
współfinansowany przez Unię Europejską
ze środków Europejskiego Funduszu Rozwoju Regionalnego
w ramach Programu Operacyjnego Innowacyjna Gospodarka, 2007–2013

Oś priorytetowa 1.: Badania i rozwój nowoczesnych technologii
Działanie 1.3.: Wsparcie projektów B+R na rzecz przedsiębiorstw realizowanych przez jednostki naukowe
Poddziałanie 1.3.1.: Projekty rozwojowe
Rekomendowana kwota dofinansowania: 3 391 950,00 PLN
Termin realizacji projektu: 01.07.2007–01.07.2013

Cele projektu:

- opracowanie innowacyjnej i ekonomicznej technologii fitoremediacji terenów zdegradowanych;
- produkcja naturalnego środka do biofumigacji gleb użytkowanych rolniczo i ogrodniczo.

Zadania badawcze projektu:

- przeprowadzanie badań fizjologicznych kapusty z upraw prowadzonych w różnych warunkach;
- opracowanie technologii uprawy kapusty;
- badania analityczne w celu określenia wpływu warunków uprawy kapusty na zawartość związków bioaktywnych i biokumulację metali ciężkich w kapuście;
- statystyczne opracowanie wyników pomiarów;
- opracowanie technologii otrzymywania biopreparatu zgodnie z wymogami przemysłu;
- zaproponowanie metod zagospodarowania odpadu po produkcji biopreparatu.

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Invitation for ECOpole ’11 Conference

CHEMICAL SUBSTANCES IN ENVIRONMENT

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

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

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

The Conference language is English.

Contributions to the Conference will be published as:

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

Additional information one could find on the Conference website:

ecopole.uni.opole.pl

The deadline for sending the Abstracts is **15.07.2011** and for the Extended Abstracts: **1.10.2011**. The actualised list (and the Abstracts) of the Conference contributions accepted for presentation by the Scientific Board, one can find (starting from 15.07.2011) on the Conference website.

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Further information is available from:
Prof. dr hab. Maria Wacławek
Chairperson of the Organising Committee
of ECOpole '11 Conference
University of Opole
email: Maria.Waclawek@o2.pl
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do udziału w Środkowoeuropejskiej Konferencji
ECOpole ’11
w dniach 12–15 X 2011

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– SIII Zarządzanie środowiskiem w warunkach kryzysowych
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