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Adam PERCZAK[1*], Agnieszka WAŚKIEWICZ[1]
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METAL POLLUTION OF SURFACE WATER FROM WIELKOPOLSKA REGION

ZANIECZYSZCZENIE METALAMI WÓD POWIERZCHNIOWYCH WIELKOPOLSKI

Abstract: Polish water resources in comparison to other European countries are small. It is one of the factors leading to increased interest in monitoring tests for their quality. Heavy metals are major water pollutants in Poland. The aim of this study was to determine seasonal variability in concentrations of cadmium, lead, zinc and copper in various reservoirs and water courses in the Wielkopolska region. Water samples were collected from lakes, large and small rivers and drainage ditches. These water bodies differ in land use in the surrounding. These were mostly rural. The study was conducted during the growing season from May to December 2012. Quantitative analysis of heavy metals was performed on the AA spectrometer Agilent 280Z. The results showed high seasonal variation in heavy metal contents in different water bodies. The concentrations of cadmium and zinc mainly depend on the date of discharge to water. Lead concentrations were caused by emissions and depended mainly on cultivation measures in fields. The highest concentration of copper was observed in the lakes, which could be due to the use of compounds that eliminate algal blooms. Under Polish law, all water bodies are classified into water quality classes I or II intended for drinking. Living conditions for cyprinids and salmonids were satisfactory in all the locations.

Keywords: heavy metals, surface waters, Wielkopolska

Introduction

The hydrosphere is struggling with surface water pollution with different undesirable substances. As a result municipal and industrial waste waters have to be treated before they may discharged into rivers and various water bodies. The main sources of water pollution include: industrial waste water discharge, discharge of cooling water from the power industry, mine water discharge, surface runoff from agricultural areas, runoff from landfills and industrial areas and pollution from precipitation [1, 2].

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Heavy metals are elements which have a specific gravity greater than 4.5 grams per cubic centimeter [3]. In various chemical reactions they tend to donate electrons to form cations. They are characterized by good electrical and thermal conductivity, have high boiling and melting points and exhibit reducing properties. They are toxic to living organisms and some of them have radioactive properties. Pollution of these elements is a worldwide problem, as they are irreducible and their accumulation at a particular place can be toxic to living organisms [4–6]. Their circulation and migration in the environment is caused by processes such as weathering of rocks, steaming oceans, volcanic eruptions or forest fires. Inorganic metal compounds are most dangerous to living organisms as they easily break down and permeate through the mucous membranes, and thus get into the internal organs. Heavy metals usually accumulate in the kidneys, liver, lungs, even in the hair and on the skin. They may cause hypertension, cancer, renal failure, brain and liver diseases, and also lead to a variety of mental disorders [7–11].

Metals in the form of cations have the ability to connect to proteins and biological tissues leading to their bioaccumulation. Each metal has a specific selectivity to connect to different tissues, for example, such as lead and radon accumulate in the bone tissue, while mercury and cadmium in the kidneys [8, 12, 13]. Metal ions bind readily with amino acids, enzymes and -SH groups. These are the active sites, causing disturbances in the functioning of many important enzymes in the body [14]. Surface waters are among the elements of the environment contaminated with heavy metals. Contamination with these elements is generally caused by anthropogenic factors. Rivers in the Upper Silesia region contain more metals than those in the northern part of the country. The Wielkopolska region is exposed to factors that increase heavy metal levels in surface waters, such as agriculture, mainly due to the chemicals used and waste discharge. Increased levels can be caused by the use of compounds to eliminate algae blooms. The presence of certain heavy metals may be caused by emissions from agricultural machines. Water reservoirs due to their location in the lowest point of the catchment area are receivers of pollutants from the whole catchment [15].

The natural content of zinc in river waters is about 10 micrograms per liter. Most inland waters are characterized by a significant content of this element, the Wistula has an average of about 20 to 180 $\mu g \cdot dm^{-3}$ [16]. Zinc toxicity in water is not high and depends on its ionic form. The concentration at 300 $\mu g \cdot dm^{-3}$ can be harmful to a variety of aquatic organisms [17].

Lead naturally occurring primarily in the form of lead (II) sulphide and it is susceptible to treatment. Its properties, however, make it toxic in situations where it is absorbed in large amounts by humans and animals. It is characterized by similar properties to calcium, which is why it is accumulated in the bones of humans and animals [18]. The lead content in unpolluted rivers amounts to micrograms per liter. In polluted waters this value can go up to tens of micrograms.

Sources of cadmium include discarded batteries, industrial and household sewage, fertilizers and plastic waste. The content of cadmium in water depends mainly on anthropogenic factors. The natural content is around 0.02 $\mu g \cdot dm^{-3}$ of water. Currently this value is exceeded in most rivers. In the Odra catchment the concentration of this element is around 1 μg · dm^{-3} [19]. As a toxic element, it usually causes pathological changes in the kidneys and lungs [7, 8, 20].

Copper is strongly bound by organic matter and clay minerals – it is precipitated as sulphides, sulphates, carbonates, etc. Copper content in the river water is about 1–2 μg · dm^{-3}. Rivers in Poland exceed this concentration, even several times. At higher concentrations this element poses a serious risk to aquatic organisms. A high concentration of copper can be detected in the vicinity of copper mines [21].

The aim of this study was to determine seasonal variability in concentrations of selected heavy metals (cadmium, lead, zinc and copper) in various reservoirs and water courses in the Wielkopolska region.

Material and methods

The experimental material consisted of water samples collected on a monthly basis from ten sites around selected ditches and ponds, which were characterized by a diversity of land uses. One of the objectives was to illustrate migration of heavy metals, mainly from agricultural areas to areas not necessarily related to agriculture. Sampling took place in the middle of each month from May to December during the growing season in 2012. Samples (about 2 dm^3) were collected using a bucket immersed to a depth of about 20 cm below the water table, which were then transported and stored in sterile canisters (refrigerated conditions) until analysis. Water samples were filtered through Filtrak no. 389 filter paper (Filtrak, Germany) and GF/B filter glass microfiber filters (Whatman, England). Quantitative analysis of copper, zinc, lead and cadmium were performed using 280Z AA spectrometer, which is designed for the determination of trace metals in the environment. Standard solutions of these heavy metals were used at a concentration of 1000 μg · g^{-1}.

For this purpose, electrothermal atomization is run in a graphite furnace with a zone of constant temperature (GTA module 120). An automatic dosing system makes it possible to adjust the sample volume of a given analyte, down to low concentrations (5–70 mm^3). The apparatus is equipped with 8 lamps and is completely automated. This is a big advantage because it allows the spectrometer to perform fast and accurate measurements.

Results and discussion

Water quality assessment indicates whether there is seasonal variability in water components and how natural land features and human activity affect those conditions. Water quality is defined in terms of its physical, chemical and biological parameters [22].

Analyses provided concentrations of selected metals in different water bodies in the Wielkopolska region.

Seasonal variation of cadmium content was observed in selected streams and reservoirs (Table 1). The highest cadmium content was observed in the Miloslawka River amounting to –0.368 μg · dm^{-3} in October while the lowest was detected in

Table 1

Seasonal variation of cadmium in water samples (three replicates for each sample) during growing season in 2012

Location	V	VI	VII	VIII	IX	X	XI	XII	Seasonal mean	Standard deviation*
	[µg · dm^{-3}]									
Jeziory Male Lake	0.001	0.130	0.164	0.257	0.174	0.199	0.135	0.123	0.148	0.074
Raczynskie Lake	0.018	0.042	0.135	0.145	0.154	0.214	0.168	0.164	0.130	0.066
Miloslawka	0.001	0.017	0.150	0.167	0.125	0.368	0.232	0.200	0.158	0.118
Maskawa	0.005	0.064	0.182	0.239	0.214	0.166	0.209	0.187	0.158	0.081
Struga Sredzka	0.008	0.133	0.208	0.275	0.261	0.205	0.115	0.176	0.173	0.087
Sredzkie Lake	0.002	0.107	0.166	0.223	0.225	0.179	0.166	0.146	0.152	0.072
Drainage ditch Lorenka	0.031	0.162	0.163	0.164	0.149	0.115	0.084	0.078	0.118	0.050
Warta the bridge of Queen Jadwiga	NT	0.053	0.150	0.185	0.244	0.168	0.163	0.142	0.158	0.057
Warta near Cytadela	NT	0.031	0.186	0.158	0.279	0.085	0.079	0.066	0.126	0.086
Bogdanka	NT	0.175	0.213	0.151	0.237	0.168	0.176	0.154	0.182	0.032

* Calculated standard deviation from the average seasonal aimed to show the seasonal variability of concentrations of heavy metals in each water sample; NT – not tested.

Table 2

Seasonal variation of zinc in water samples (three replicates for each sample) during growing season in 2012

Location	V	VI	VII	VIII	IX	X	XI	XII	Seasonal mean	Standard deviation*
	[μg · dm^{-3}]									
Jeziory Male Lake	0.907	0.121	0.088	0.195	0.155	0.455	0.421	0.332	0.334	0.269
Raczynskie Lake	0.907	0.098	0.156	0.023	0.155	0.451	0.425	0.156	0.296	0.289
Miloslawka	0.913	0.013	0.059	0.065	0.047	0.401	0.387	0.210	0.262	0.305
Maskawa	0.940	0.077	0.172	0.031	0.154	0.423	0.401	0.316	0.314	0.291
Struga Sredzka	0.933	0.005	0.157	0.036	0.095	0.444	0.409	0.303	0.298	0.305
Sredzkie Lake	0.843	0.204	0.083	0.124	0.067	0.415	0.408	0.392	0.317	0.258
Drainage ditch Lorenka	0.783	0.060	0.124	0.012	0.033	0.401	0.386	0.274	0.259	0.262
Warta the bridge of Queen Jadwiga	NT	0.069	0.047	0.039	0.113	0.365	0.323	0.313	0.181	0.145
Warta near Cytadela	NT	0.064	0.043	0.021	0.089	0.395	0.375	0.218	0.172	0.159
Bogdanka	NT	0.082	0.035	0.019	0.099	0.417	0.410	0.402	0.209	0.190

* Calculated standard deviation from the average seasonal aimed to show the seasonal variability of concentrations of heavy metals in each water sample; NT – not tested.

Table 3

Seasonal variation of lead in water samples (three replicates for each sample) during growing season in 2012

Location	V	VI	VII	VIII	IX	X	XI	XII	Seasonal mean	Standard deviation*
	[μg · dm^{-3}]									
Jeziory Male Lake	0.210	0.581	1.085	2.797	1.172	30.626	12.584	12.084	7.643	10.596
Raczynskie Lake	0.180	0.765	1.633	0.344	0.833	32.182	6.882	5.138	5.995	10.863
Miloslawka	0.323	0.794	1.708	1.395	1.823	8.119	0.198	0.086	1.806	2.640
Maskawa	0.966	2.032	1.661	0.964	2.012	36.769	36.472	32.528	14.176	17.507
Struga Sredzka	0.430	0.893	1.526	0.835	1.568	51.470	27.077	22.158	13.245	18.809
Sredzkie Lake	0.380	1.325	1.034	0.797	2.325	31.272	20.777	18.853	9.596	12.174
Drainage ditch Lorenka	0.206	1.366	1.052	0.828	6.024	68.000	32.130	28.951	17.320	24.304
Warta the bridge of Queen Jadwiga	NT	0.896	1.087	0.848	26.326	33.076	14.603	10.112	12.421	13.072
Warta near Cytadela	NT	0.894	1.246	0.786	30.769	33.747	22.073	18.742	15.466	14.450
Bogdanka	NT	1.269	1.307	0.755	10.258	12.547	25.934	20.185	10.322	10.006

* Calculated standard deviation from the average seasonal aimed to show the seasonal variability of concentrations of heavy metals in each water sample; NT – not tested.

Table 4

Seasonal variation of copper in water samples (three replicates for each sample) during growing season in 2012

Location	V	VI	VII	VIII	IX	X	XI	XII	Seasonal mean	Standard deviation*
	[μg · dm^{-3}]									
Jeziory Male Lake	4.096	19.523	31.630	29.960	26.346	5.846	0.490	0.444	14.792	13.492
Raczynskie Lake	6.073	17.646	30.980	26.135	25.103	24.198	3.788	3.025	17.119	11.250
Miloslawka	9.056	11.603	15.493	14.322	7.530	5.029	3.021	2.873	8.616	4.889
Maskawa	5.936	15.433	15.746	13.750	7.766	2.903	4.135	4.012	8.711	5.417
Struga Sredzka	4.700	12.846	14.616	13.893	7.851	2.560	0.666	0.602	7.217	5.930
Sredzkie Lake	4.820	50.080	22.117	18.473	11.560	4.405	0.681	0.557	14.087	16.596
Drainage ditch Lorenka	1.483	6.326	13.936	11.330	10.826	3.481	0.309	0.223	5.990	5.442
Warta the bridge of Queen Jadwiga	NT	16.783	17.670	18.816	16.643	0.646	0.423	0.409	10.199	9.107
Warta near Cytadela	NT	19.086	18.190	15.960	10.315	1.708	0.108	0.994	9.480	8.476
Bogdanka	NT	11.656	29.996	27.180	18.753	6.028	1.515	1.054	13.741	11.862

* Calculated standard deviation from the average seasonal aimed to show the seasonal variability of concentrations of heavy metals in each water sample; NT – not tested.

a drainage ditch Lorenka at 0.164 μg · dm^{-3}. The highest seasonal average cadmium content was observed in the Bogdanka at 0.182 μg · dm^{-3} of water, whereas it was lowest in the drainage ditch Lorenka at 0.118 μg · dm^{-3}. Seasonal variation of zinc was also observed in selected streams and reservoirs. The highest zinc content was recorded in the Maskawa at 0.940 μg · dm^{-3} in May, it was lowest in the Struga Sredzka at 0.005 μg · dm^{-3} in June. The highest seasonal average zinc content was recorded in Lake Jeziory Male at 0.334 μg · dm^{-3} of water and the lowest in the Warta River in two sampling sites, where values did not exceed 0.200 μg · dm^{-3} (Table 2). Lead concentration is also marked by seasonal variation. The highest content was observed in the drainage ditch Lorenka at 68 μg · dm^{-3} in October, the lowest in Miloslawka at 0.086 μg · dm^{-3} in December (Table 3). The highest seasonal average lead content was recorded in the drainage ditch and it amounted to 17.320 μg · dm^{-3} of water, while it was lowest in the Miloslawka at 1.806 μg · dm^{-3}. Copper also showed seasonal variation. The highest copper content was detected in Lake Sredzkie at 50.080 μg · dm^{-3} in June, whereas it was lowest in the Warta River at a sampling point near Cytadela Park, amounting to 0.108 μg · dm^{-3} in November (Table 4). The highest seasonal average cadmium content was recorded in Lake Raczynskie at 17.119 μg · dm^{-3} of water, while it was lowest in the drainage ditch Lorenka amounting to 5.990 μg · dm^{-3}. Standard deviation of the seasonal means was calculated to show seasonal variability in concentrations of selected elements in the study areas.

Correlation coefficients between groups were determined in order to examine the relationship between seasonal variability in heavy metal concentrations (Table 5). For this purpose first the mean values of all intake levels were calculated for each month. In the next stage, the correlation coefficients were determined for each group of heavy metals.

Table 5

The correlation coefficients between selected heavy metals

Metals	Cd	Zn	Pb	Cu
Cd	1			
Zn	–0.714	1		
Pb	0.365	0.177	1	
Cu	0.268	–0.686	–0.654	1

High negative correlation values were found between cadmium and zinc (r = –0.714), copper and zinc (r = –0.686), and copper and lead (r = –0.654).

Contents of various heavy metals are influenced by agriculture and mining (Table 6). Different countries face the problem of high heavy metal concentrations in different water bodies inhabited by living organisms. The purpose of monitoring is to show which pollution has to be dealt with and verify the main causes of their occurrence. The following table shows examples observed worldwide that illustrate the content of heavy metals in water in the different continents.

Admissible concentrations of heavy metals are exceeded in rivers and lakes in the Wielkopolska region. Relatively high values have been shown for copper and lead,

Table 6

Concentration of heavy metals in different water reservoirs in various countries

Locations	Country	Concentration of heavy metals [$\mu g \cdot dm^{-3}$]				References
		Zinc	Lead	Copper	Cadmium	
Wielkopolska region	**Poland**	**< 1.000**	**< 70.000**	**< 50.000**	**< 0.370**	**our studies**
Brahmani river	India	80.100	27.000	4.700	4.000	[23]
Changijang river	China	18.750	6.400	8.400	0.300	[24]
Han river	China	NT	9.260	13.350	2.310	[25]
Ataturk Dam lake (Adiyaman)	Turkey	0.197	NT	0.220	NT	[26]
Manchar lake	Pakistan	79.200	19.780	23.140	6.620	[27]
Brzezno lake	Poland	12.450	10.305	3.950	1.300	[28]
Radun lake	Poland	6.550	16.500	4.250	1.300	[28]
Mlosino Wielkie lake	Poland	3.950	13.150	1.400	2.000	[28]

NT – not tested.

which reached maximum values of 50 and 70 μg · dm^{-3}, respectively. Different literature sources published worldwide show how industrialization affects the relevant heavy metal concentrations in surface waters. In India in the Brahmani River [23] high concentrations of zinc and cadmium (corresponding to 80 and 4 μg · dm^{-3}) were reported. Content of lead and copper were lower than in the waters of the Wielkopolska region. In Chinese rivers, the Changijang and the Han [24, 25] lower concentrations of lead and copper were also reported (max. 9 and 13 μg · dm^{-3}). The Han River had a higher concentration of cadmium (2.3 μg · dm^{-3}), while in the Changijang it was for zinc (18.75 μg · dm^{-3}). In the Turkish Ataturk Dam lake [26] in Adiyaman much lower zinc and copper concentrations were showed than it was in the Wielkopolska region (approximately 0.2 μg · dm^{-3}). The Manchar lake [27] is characterized by higher concentrations of zinc and cadmium (up to 80 and 6.6 μg · dm^{-3}, rerspectively). In Poland tests are also carried out to monitor the concentrations of heavy metals in surface waters. In lakes Brzezno , Radun and Mlosino Wielkie [28] lower levels of lead and copper were reported (up to 16.5 and 4.25 μg · dm^{-3}, respectively) together with higher amounts of zinc and cadmium (up to 12.45 and 2 μg · dm^{-3}, respectively). In another study conducted by Antonowicz (2008) within a 24 h period daily changes in the concentrations of lead, zinc, cadmium, manganese and copper were analyzed in surface microlayers and in subsurface water of Lake Gardno. It was observed that concentrations of these metals both in surface microlayers and in subsurface water within 24 h show considerable variation, resulting from transport processes in the vertical profile of a water column [29]. Moreover, Antonowicz and Trojanowski tested the effect of salinity level on the concentration of cadmium and manganese in the surface microlayer in Lake Gardno [30]. Cadmium accumulation in microlayers of surface waters in Lake Gardno was dependent on the concentration of this metal in the deep waters and varied with water salinity, while both metal levels in analyzed surface water microlayers were higher than in the subsurface layer [30].

Conclusions

1. Seasonal variability of cadmium and zinc depend on the date of discharge to water, and the use of chemical fertilizers in crop fields.
2. The concentration of lead in water resulted from emissions and reached its peak in October (up to 60 μg · dm^{-3}), due to the greater impact of crop fields during this period.
3. The highest copper content recorded in the lakes was probably caused by the compounds used to eliminate algae blooms.
4. According to the Regulation of the Minister of the Environment of 27 November 2002 on the requirements to be met by surface water used for public supply of water intended for human consumption, water samples in all the analyses, in terms of heavy metals have been classified to classes I or II.
5. According to the Regulation of the Minister of the Environment of 4 October 2002 on the requirements to be met by inland waters that are the habitat of fish in the wild, satisfactory living conditions for salmonids and carp were found in all tests.

6. Negative correlations were found between the content of cadmium and zinc (r = –0.714), copper and zinc (r = –0.686), as well as copper and lead (r = –0.654).

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ZANIECZYSZCZENIE METALAMI WÓD POWIERZCHNIOWYCH Z TERENU WIELKOPOLSKI

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Abstract: Zasoby wodne Polski w porównaniu do innych krajów europejskich są małe. Jest to jeden z czynników powodujących wzrost zainteresowania badaniami monitoringowymi dotyczącymi ich jakości. Jednym z istotnych zanieczyszczeń są metale ciężkie. Celem pracy było określenie sezonowej zmienności stężeń kadmu, ołowiu, cynku oraz miedzi w różnych zbiornikach i ciekach wodnych z terenu Wielkopolski. Brano pod uwagę takie źródła poboru jak jeziora, duże i małe rzeki oraz rowy melioracyjne. Miejsca poboru charakteryzowały się zróżnicowaniem użytkowania terenów występujących wokół nich. Były to głównie tereny rolnicze. Badania przeprowadzono w sezonie wegetacyjnym od maja do grudnia 2012 roku. Analizę ilościową metali ciężkich wykonano na spektrometrze 280Z AA firmy Agilent. Uzyskane wyniki wykazały dużą sezonową zmienność występowania metali ciężkich w różnych zbiornikach wodnych. Stężenie kadmu i cynku zależało głównie od terminu zrzutu ścieków do wód. Poziom stężeń ołowiu ukształtował się w wyniku emisji spalin i zależały głównie od ingerencji maszyn rolniczych na polach uprawnych. Najwyższe stężenia miedzi odnotowano w jeziorach, co mogło być spowodowane zastosowaniem związków eliminujących zakwity glonów. Zgodnie z polskim prawem, wszystkie miejsca badawcze zostały zaklasyfikowane do I lub II klasy jakości wód przeznaczonych do picia. We wszystkich miejscach były spełnione warunki do życia ryb karpiowatych i łososiowatych.

Słowa kluczowe: metale ciężkie, wody powierzchniowe, Wielkopolska

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EFFECT OF "HAJDOW" WASTEWATER TREATMENT PLANT MODERNIZATION ON WASTEWATER PURIFICATION PROCESS

WPŁYW MODERNIZACJI URZĄDZEŃ MIEJSKIEJ OCZYSZCZALNI ŚCIEKÓW „HAJDÓW" NA PRZEBIEG PROCESU OCZYSZCZANIA

Abstract: The study presents the effect of modernization of selected elements of the technological line in the 'Hajdów' municipal wastewater treatment plant (WWTP) on the course of the process of wastewater treatment. The researchers paid special attention to the changes in the amount of emerging waste (rake bar screens, sand, excess sludge) due to modernization, and the elimination of odour nuisance from the plant. Technological changes in the system of activated sludge bioreactor contributed to a considerable increase in the amount of excess sludge. This caused problems with its effective management with the use of previously applied methods and devices; therefore, facilities were introduced supporting the dehydration of excess sludge. Therefore, the article also presents the description of solutions concerning the processing of sludge introduced to-date in the 'Hajdów' WWTP and further modernizations implemented.

Keywords: activated sludge, sludge management, odour nuisance, biofilters, WWTP modernization

Introduction

Research Poland's accession to the European Union resulted in the necessity for adjustment of Polish law to the Community law. The Accession Treaty assumes the full implementation of the Directive 91/271/EEC of 21 May 1991 (with later amendments)

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by 31 December 2015, with transitional periods during 2005, 2010, 2013 (reporting to the European Commission) [1]. If the obligations arising from the Directive are not fulfilled within the specified terms, the European Commission (EC) may issue a complaint to the European Court of Justice, and then impose financial penalties on the member states. The basic instrument for the implementation of the provisions of the Directive 91/271/EEC is the National Programme for Municipal WWTP [2]. The Directive regulations were transposed into Polish law, among others, in: the Act in the matter of collective water supply and collective wastewater discharge, the Water Act, or the Regulation by the Minister of Environment of 24 July 2006 in the matter of conditions to be fulfilled while discharging wastewater into waters or soil, and in the matter of substances especially hazardous for the water environment [3–10].

Therefore, the modernization of the wastewater treatment plant all over the world has become necessary in order for it to function in accordance with the provisions of the law, and that transgressions of the law do not result in financial penalties [11]. In addition, ways to improve the performance of wastewater treatment is very much and they are not just reconstruction or expansion of existing facilities as well as the introduction of new or alternative technologies [12–15].

The modernization of the plant results also from the fact that the unit's function in constant contact with wastewater exerting an aggressive effect, and relatively quickly become used. As a result of modernization, the treatment plant is becoming increasingly more environmentally friendly, its odour nuisance decreases, and the effectiveness of wastewater treatment increases. Thus, for more than a dozen years the 'Hajdów' wastewater treatment plant has been undergoing subsequent modernizations in order not to deviate from the European standards of wastewater treatment.

The 'Hajdów' wastewater treatment plant is a mechanical-biological facility using activated sludge technology, to which enter sanitary and industrial wastewater from the Lublin agglomeration (Lublin, Świdnik, Wólka, Konopnica). In the first half of the 2014, the amount of the influent was approximately 60 174 m^3/daily on average [17,18]. The effluent is discharged into the Bystrzyca River. The treatment plant was designed in the 1970s, and its construction lasted until 1992.

The process of wastewater treatment consists of mechanical and biological parts. In the mechanical part, wastewater flows subsequently through the screens, grip chamber and preliminary settling tanks. At this stage, rakings, sand and raw sludge are trapped. Suspensions which are difficult to settle and dissolved substances are removed in the biological part of the treatment plant. Purification is performed in bioreactors with activated sludge, which function in a modified Bardenpho system for the removal of carbon, nitrogen and phosphorus compounds. After the process of treatment in bioreactors, wastewater is separated from secondary sludge in secondary settling tanks [17–20]. Sludge emerging in the processes of wastewater treatment is subjected to fermentation in selected fermentation chambers (SFCs), and subsequently mechanically dehydrated on belt-filter presses. Dehydrated sludge is subjected to the process of thermal drying. In the WWTP, three lines of fluidized bed pneumatic dryers are installed. The use of this technology allows the hygienization of sludge, reduction of the mass and volume of sludge by several times and, in consequence, a reduction in the

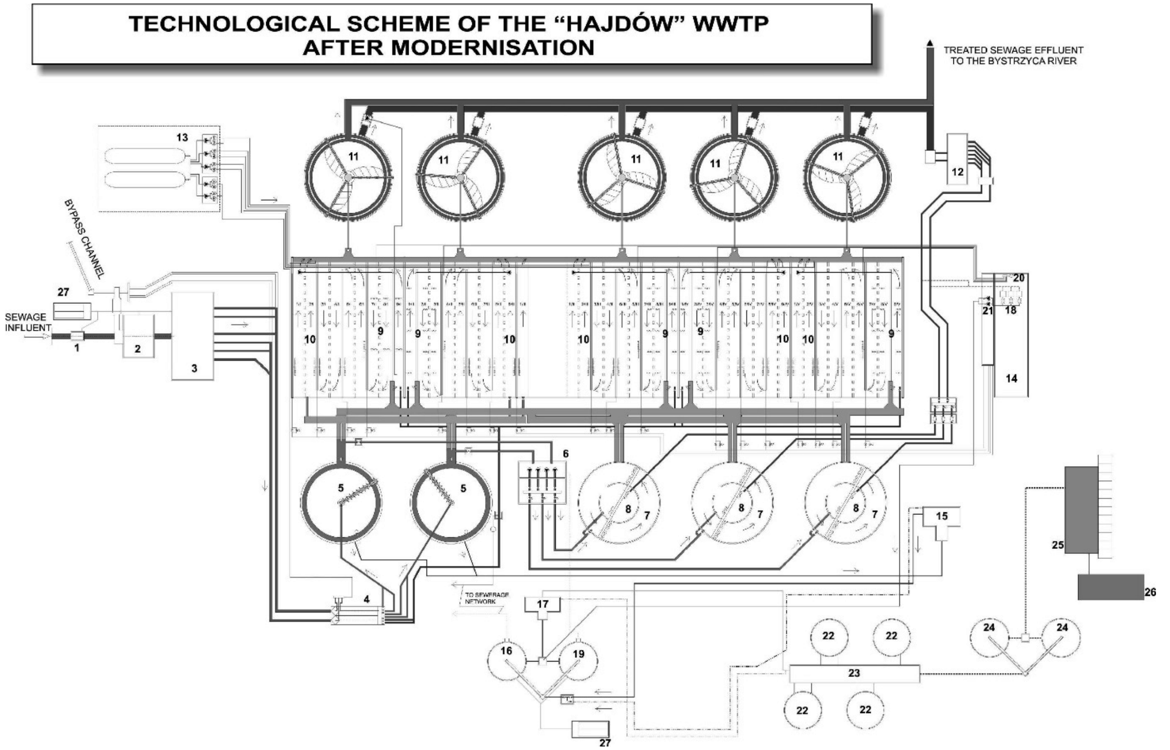

Fig. 1. Technological scheme of ‘Hajdow’ wastewater treatment plant in Lublin
Legend: 1. Venturi tube in open channel, 2. Screens 3. Main pumping station 4. Aerated sand trap 5. Primary settling tanks 6. Intermediary pumping station 7. Anaerobic chambers 8. Return sludge pre-denitrification chambers 9. Denitrification chambers 10. Nitrification chambers 11. Secondary setting tanks 12. Return sludge pumping station 13. PIX preparation and dosing station 14. Blowers station 15. Primary raw sludge pumping station 16. Primary sludge thickener 17. Thickened sludge pumping station 18. Sludge mechanical thickening station 19. Sludge digester 20. Flocculent preparation and dosing station 21. Thickened surplus sludge pumping station 22. Closed digestion chambers 23. Operational building 24. Digested sludge thickeners 25. Mechanical dewatering sludge station 26. Thermal drying station for the dewatered sludge 27. Biofilter [3]

costs of transport and potential storage of waste. After drying, the sludge is destined for economic use – as an alternative fuel or component of mineral-organic fertilizer.

As a result of the methane fermentation process, biogas is produced which, in a modernized heat and power station, is used for the production of thermal and electric energy. The thermal energy produced fully covers the demand of the treatment plant, while electric energy covers approximately 14 % of the plant's demand. Biogas is also used as fuel in the process of drying of sludge in fluidized bed dryers. Figure 1 presents the scheme of the mechanical-biological 'Hajdow' wastewater treatment plant in Lublin.

Considering the progress in the technology of wastewater treatment, changes of legal regulations, and changes in the amount and composition of influent wastewater the modernization has become necessary of both the devices and technologies used in the treatment plant. The first modernization undertakings began soon after its start-up. It should be noted that the latest modernization was co-financed from the European Union resources.

Modernization of rake bar screen

The first unit in the technological line of wastewater treatment is the rake bar screen. Initially, a bar screen was installed made of ordinary steel, with spacing of 20 mm. The system of transport of disposed contaminants consists of an unshielded conveyor and trolley, which conveys wet screenings to the height of 8 m into an open container. The modernization of the bar screen is accompanied by a change in the technology of dehydrating and transporting of screenings within the unit.

In 1996, old bar screens were removed, and replaced by step bar screens with bar spacing of 5 mm, produced of stainless steel. For the transport of screenings, four band conveyors were used which by means of rotating spirals enabled the transport of wet materials (hygienically dangerous) at various angles and at considerable heights, simultaneously providing total hermetic sealing of the system. A press was also installed allowing a decrease in the hydration of screenings, equipped with a hermetic shield. Dehydrated screenings from the conveyor are transported into a closed container via two plastic sleeves. In order to suppress emission of odour nuisance from the container, a ventilation duct was additionally installed, attached to negative pressure ventilation. This system also collects contaminated air from the shielded screens and carries it away to the biofilter, where purification takes place [18].

In 2012, the bar screens and the system of transport of screenings were modernized once again. In the screen bar unit, four conveyor rake sieves with hook-like plates were installed with spacing of 6 mm. These sieves provide a greater separation of screenings (especially fibrous contaminants), and the screenings washing presses guarantee a high degree of washing away of dissolved organic substance and the reduction in the amount of screenings. These presses function automatically according to the level of wastewater in front of the screen. Screenings captured on the bar screens are transported by a system of horizontal and vertical screw conveyors through two washing presses into the container. Similar to the last modernization, the air from all nuisance odour units is carried away to the biofilter. The biofilters were started up in 2002 and function to-date.

Figure 2 presents changes in the amounts of screenings retained in the subsequent years. Directly prior to modernization the amount of contaminants retained on screens was 336 Mg annually, while a year later this was as much as over 1100 Mg annually. In 2013, the amount of retained screenings was 577.74 Mg annually.

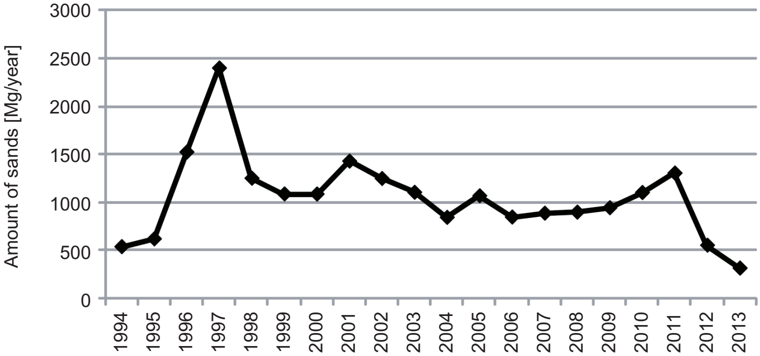

Fig. 2. Amount of screenings retained prior to and after modernization in 1996 and 2012 [3, 6]

Modernization of sand washer

Wastewater pumped from the grates by means of an intermediate pumping station are transported into two distribution chambers, from which through a system of valves may be directed to each of the four funnels of the sand washer. In order to improve the effect of sand removal, the funnels are aerated with compressed air from the blower station.

Modernization of the sand washer consisted in replacing the former pump-hydrocyclon system by light bridges with suspended floodable pumps [19]. Sand hydrated by the pumps is transported into a gutter and stationary separator; therefore, it was possible to cover the sand washer with polyester-glass laminate plates over the wastewater mirror. All construction elements in contact with wastewater were made of stainless steel.

In 2012, during the modernization of the sand washer, Zickert scrapers and sand separator were installed. Sand retained at the bottom is removed to the sand hopper by four bottom scrapers placed in each chamber of the sand washer. From each hopper, sand is removed by means of a pump, then directed to the separator, from where it is transported to the container. The use of the separator with a grit washer allowed for the separation of organic matter from the sand (organic substance returns to the process of purification), which significantly reduced the amount of the removed sand.

Figure 3 presents changes in the amount of sand removed in the subsequent years. Before modernization, the amount of the sand removed was 616.40 Mg annually, whereas after modernization – approximately 2400 Mg annually. In 2012, after

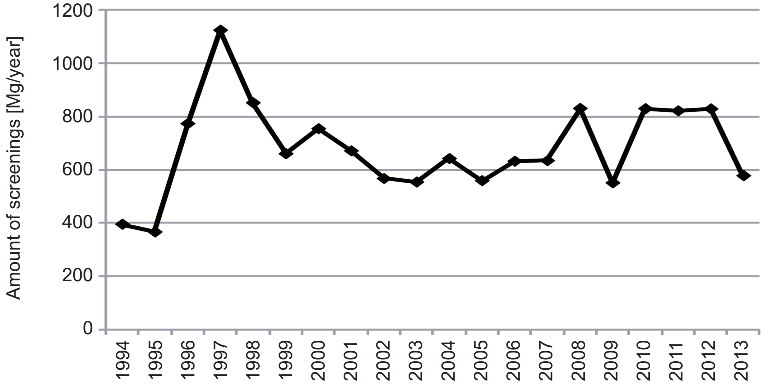

Fig. 3. Amounts of sand removed prior to and after modernization in 1996 and 2012 [3, 6]

installation of the sand separator, the amount of sand removed was 550 Mg annually, while a year later, in 2013 – 311.28 Mg annually.

Sealing of wastewater treatment plant units

For a long time, problems related with suppression of odour nuisance in the units of wastewater treatment plants had been noticed by the authorities in West European countries. In these countries, the regulations univocally indicate that the odour quality of the air is an important element of the environment [21–31]. The Municipal Enterprise for Water Supply and Sewage Systems in Lublin has undertaken a number of investments and organizational undertakings in order to solve this problem.

Firstly, the units within the wastewater treatment plant which were most noxious with respect to odour were sealed: measurement reducers chamber, emergency outflow chamber, rake bar screen, wastewater pump chamber, sand washer, and raw sludge densifier.

Measurement reducers were hermetically sealed in 1995, and modernized in 2009. The modernization consisted in reconstruction of the Venturi KPV-XI reducer for the KPV-IX reducer, and reconstruction of sewage collectors at the rake bar screen and emergency outflow chamber.

The measurement reducers chamber was covered by three domes made of polyester-glass laminate (with inlet and revision slots), based on a reinforced concrete construction of the chamber. The emergency outflow chamber was covered with two domes supported on a reinforced concrete foundation [18]. Hermetic sealing of the densifiers of raw sludge was performed by covering them with laminate elements, supported on separate foundations and suspended on a steel construction.

The glass laminate applied is resistant to atmospheric conditions and the effect of chemical agents produced during the processes of water treatment; simultaneously, this material is light and easy to form. The rake bar screen building was subjected to the previously described modernization and hermetic sealing. The construction of new rakes limits the emission of odours into the atmosphere. Also, the hermetic sealing of the transport of screenings into a closed container was applied.

The sealing also covered the densifiers of raw sludge and a fermenter, as well as densifiers of fermented sludge, buffer tanks, press station, and preliminary settling tanks, from which the odour nuisance is directed into a biofilter.

Sealing of the grit chamber was performed using panels made of synthetic materials. However, considering the small volumes of the hermetically sealed elements, only the sealing of the grit chamber was performed, without carrying away the air to the biofilter.

The last sealed unit in the mechanical part of the wastewater treatment plant are sawtooth weirs of preliminary radial settling tanks. It was decided to make covers of glass laminate for these elements, considering both the odour nuisance of mediocre intensity occurring at this place, and considerable amounts of aerosols produced.

Odour nuisance from the sealed units is directed via a special ventilation system into the biofilter. Microorganisms settling in the biofilter decompose the odour nuisance gas substances, while the purified air is released into the atmosphere through the uncovered upper surface of biofilter filling [18].

The following biofilters are used in the wastewater treatment plant:

– Biofilter I – neutralizing odour nuisance from the following units: measurement reducers chamber, emergency outflow chamber, emergency hatch chambers, rake bar screen, and wet well in raw wastewater pump-room.

– Biofilter II – neutralizing odour nuisance of the air from preliminary sludge densifiers covered by a conical laminate cover.

– Biofilter III – for the removal of odour nuisance gas at buffer tanks.

– Biofilter IV – at preliminary settling tanks which purifies the air carried away from the roofed volumes over the sawtooth outflows.

– Biofilter V – at the sludge dehydration station, purifying the air from the following units of the thermal dehydrated sludge drying station, purifying the air from the following units: dehydrated sludge buffer tank, system of dehydrated sludge conveyers, hermetically sealed presses at the sludge dehydration station, and three lines for sludge drying, three silos of dried sludge granulate.

– Biofilter VI – installed at fermented sludge densifiers.

According to the design assumptions, which have been confirmed by preliminary studies, the reduction of odour nuisance was obtained in 90 %. As a result of these investments, the state of occupational safety and work hygiene in the wastewater treatment plant has improved. Modernization contributed to both an improvement in the work conditions of employees operating and maintaining the units of the plant, as well as the reduction in complaints of the inhabitants from the nearest surroundings of the plant, which allowed avoidance of the creation of a protective zone around the WWTP.

Modernization of biological part

Bioreactors have been modernized within the investment co-financed from the resources of the Instrument for Structural Policies for Pre-Accession (ISPA).

The process of biological treatment of wastewater in the treatment plant described is based on the modified Bardenpho system (system of integrated disposal of carbon, nitrogen and phosphorus compounds). The system consists of a chamber of anaerobic activated sludge (created after the reconstruction of the preliminary settling tank, which performs the function of mixing wastewater after mechanical treatment with activated sludge, as well as the function of a prenitrification chamber and a block with distinguished zones: anaerobic, anoxic-aerobic, and secondary settling tank. Figure 4 presents the scheme of the division of a single reactor into blocks.

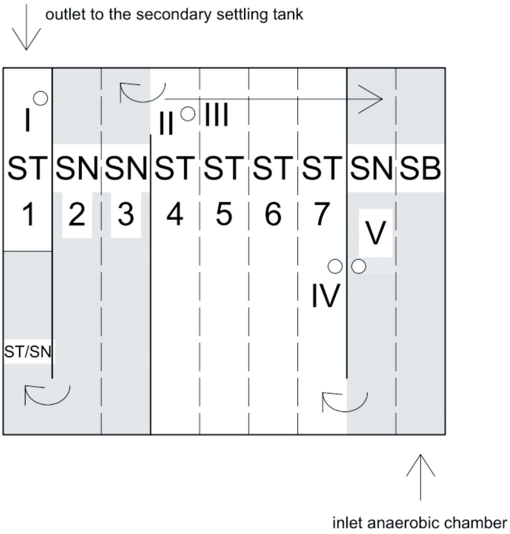

Fig. 4. Scheme of division of a single bioreactor into zones [3] ST – aerobic zone, SN – anoxic zone, SB – anaerobic zone, I – online measurement of N-NH_4, N-NO_3, sludge concentration, pH, II – alternative measuring location, III – internal recirculation, IV – online measurement of O_2, V – measurement of redox and O_2

The detailed division of the biological reactor block depends on transformations and the existing conditions, and covers several zones: the first zone (chamber) with anaerobic conditions, the second zone for preliminary nitrification, followed by four nitrification zones, the subsequent two zones, where the second-step of the nitrification process takes place, and the last chamber, which is divided into two parts: the first part serves a dual purpose – nitrification or denitrification, while in the second part, the ultimate nitrification process takes place. Thus, summing up, it may be considered that the biological part of the treatment plant, which functions as a five-step modified Bardenpho system, consists jointly of seven zones operating in series, with two of them placed in the spaces created after the reconstruction of the settling tanks, while the subsequent five zones – in modified chambers of the blocks in the aeration chambers. The internal recirculation required in the system takes place from the end of the first stage of nitrification (ST 4) until the initial area of preliminary (SN 8), the nitrification stream usually oscillates within 250 % of the amount of inflowing raw wastewater.

Modernization of the biological part of the WWTP consisted in up-dating the technologies used, which allowed the obtaining of the quality of wastewater treatment adjusted to the EU requirements. The reduction of the level of biogenic compounds has been achieved by construction of new pipelines transporting wastewater to the preliminary settling tanks, modernization of primary settling tanks, adaptation of three settling tanks to the function of an anaerobic chamber, modernization and re-construction of aeration chambers in order to adjust them for carrying out the processes of nitrification and denitrification, and biological dephosphatation. All units have been equipped with adequate sensors for on-line measurements of the key parameters, which provide information concerning the course of treatment processes: dissolved oxygen, redox, $N\text{-}NH_4$, $N\text{-}NO_3$, pH, and concentration of activated sludge. The above-mentioned measurement sensors are connected with the Supervisory Control And Data Acquisition (SCADA) system functioning in the WWTP. Also, an installation for chemical removal of phosphorus has been installed. The completion of the above-mentioned tasks enabled an improvement in the efficacy of disposal of carbon, nitrogen, and phosphorus compounds.

The process of phosphorus removal by the chemical method based on coagulating reagent dosing is providing as additional, applied exceptionally only in emergency situations. Coagulant is added to sewage leaving the nitrification and denitrification chambers. In order to cause primary sedimentation in preliminated settling tank, coagulant is dosed to the grit chamber.

The main elements of the dosing station are: storage tank, tank tray and dosing system. PIX-113 is a coagulant used in this station. PIX is a non-organic coagulant based on Fe^{3+}, in the form of a water solution of iron (III) sulfate.

Modernization of sewage sludge processing units

The first investment within the units for sewage sludge processing was the construction of the station for mechanical dehydration of fermented sludge in 1993. At this station, four belt-filtration presses were installed with a total efficacy of approximately 42.5 m^3/h. Sludge is directed to the presses from fermented sludge densifiers via screw pumps. Parallely, an organic flocculant is added in order to support dehydration. Dehydrated sludge is transported by conveyers to the drying station, or to containers placed below the last conveyer. After installation of the presses, the volume of sludge decreased from 600 m^3 daily down to approximately 80 m^3 daily, and its hydration was reduced from approximately 95–97 % down to about 80 %.

In 2003, an excess sludge densification station and a fermenter were started-up. It was decided to choose such a solution because as a result of changes in the technology of biological treatment, the amount of excess sludge produced considerably increased. Therefore, it became necessary to construct a station for the mechanical densification of sludge [5]. The station consists of two conveyor densifiers with an installation for digestion and dosing of flocculant. The use of this solution allowed the reduction in the content of water in sludge from 99.5 % down to 95 %, which means a considerable decrease in its volume by approx. 8–10 times. The mean daily amount of excess sludge currently conveyed to the densification station is approx. 3000 m^3 daily, while the average amount of sludge outgoing for further processing is approx. 370 m^3 daily (mean values acc. to data of 2005). According to the data of 2013, the mean daily amount of excess sludge was approximately 2400 m^3/daily, whereas the amount of sludge outgoing for further processing – approximately 340 m^3/daily. According to the data of the first half of 2014, the mean amount of excess sludge was 2000 m^3 daily, while the amount of sludge outgoing for further processing – 280 m^3/daily.

During modernization, one of the densifiers of raw sludge was converted into a sludge fermenter for the production of volatile fatty acids necessary for the intensification of the processes of phosphorus and nitrogen removal in the biological part of the plant. The designed fermentation time is four days for 170 m^3/daily of raw sludge. Sludge supernatant from the fermenter is carried to the wastewater wet well in the intermediate pumping station.

In 2008, a station for the thermal drying of sludge was started up, which was attached to the existing sludge dehydration station. In the thermal drying station, three lines of pneumatic dryers were installed with the fluidized bed and sludge feeding substation and silos for granulate (dried sludge).

Sediment in presses in the amount of approximately 96.27 tons daily is hydrated in about 79.7 %, and contains in the dry mass approximately 59.4 % of organic substances. The dryers allow the drying of sludge to the level of over 95.3 % dry mass.

A fluidized bed dryer is divided with a fluidized mesh into: blowing chamber, drying chamber, and air chamber placed above the drying chamber.

Each technological line for drying is composed of the following units:

– Pump supplying feed from the buffer tank to the dosing devices of the drying line (fixed at the bottom of buffer tank);

– Technological dehydrated sludge pipelines with fittings and measurement equipment;

– Fluidized dryer;

– Two air heaters of power 800 kW each, with modulating burners for the combustion of GZ50 and biogas;

– Blowing ventilator with stepless blow control.

The capacity of each line is 1.5 Mg/h of evaporated water.

The drying agent is air at a temperature of approximately 130 ^{o}C, heated in the thermal centre using a gas burner. The fuel is petroleum gas or biogas. The result of drying is a granulate with a grain size of several millimeters. The constructed installation enables the drying of about 4 Mg/h of sludge with dry mass up to 25 %. As a result of this process, approximately 92 % of dry mass is obtained, and the expected operation time of the installation is about 8000 hours annually.

Modernization of separated fermentation chambers (SFCs) with the operations building and biogas tanks

The SFCs functioning in the ‘Hajdow’ WWTP are closed tanks made of reinforced concrete for the single-stage mesophilic fermentation of sludge. They are made of reinforced concrete. The middle part has a cylindrical shape, while the upper and bottom parts – the shape of a cone. Densified sludge inflows subsequently into each of four tanks. Prior to modernization, the mixing of the content of the chambers, together with preheating of sludge in heat exchangers, took place by means of circulation pumps and heat exchanges located in the operation building. The heating agent was water at the temperature of 76 ^{o}C, supplied from the gas boiler. A separate pump was used for breaking the scum forming in the SFC, which pumped sludge over the upper level of sludge in the SFC, and as a result of outflow through four nozzles flooded the forming scum.

The drainage of fermented sludge took place by means of a telescopic spillway or by opening the valve on the drain pipeline. An emergency spillway secures against exceeding the upper maximum level of sludge in the chamber. The level of sludge in SFC was measured using isotopic level indicators.

Biogas produced during fermentation was handled using a gas catcher with water lock, and discharged to the sulphur recovery system and gas tank.

At present, modernization is ongoing of selected fermentation chambers, which covers the change of the method of mixing sludge (from that previously used by means of pumps, to mixing with a mixer with a central pipe forcing sludge flow), heating, breaking scum and slaking foam. New pumps, fittings, and gas uptake will be installed. Also, new homogenization and excess sludge disintegration units will be installed, which will increase the susceptibility of sludge to fermentation. Disruption of fluff and microorganisms present in sludge will increase the availability of the organic substance during the fermentation process. It is expected that modernization will result in an increase in biogas production, increase in the degree of sludge mineralization, reduction of fermentation time, and increase in the degree of dehydration of sludge, which in consequence, may decrease the amount of sludge for management and contribute to the minimization of the costs of its processing and utilization.

Before modernization, steel tanks for biogas were installed in the treatment plant, which served for the storage of biogas produced in SFC, and to equalize the pressure of gas during the drainage of sludge from SFC. The pant possessed two steel tanks of the volume of 2000 m^3 each. Each tank consisted of a water pond and a mobile segment filled with gas (bell).

At present, tanks made of plastic are installed in the treatment plant. The biogas tank consists of two membranes: external (protective) and internal (storage). The bottom part of the storage membrane also seals the biogas tank on the part of the baseplate. The pressure in the tank and the state of constant tension of the external membrane is obtained by the functioning of an air ventilator placed on a baseline directly at the biogas tank.

Production of biogas

The possibilities of using biogas are limited by the high concentration of hydrogen sulphide (3.89 g H_2S/m^3 biogas) (exceeding allowable values for heating equipment and generators). Table 1 presents the composition of biogas produced in the wastewater treatment plant. Until 2008, the removal of sulphur from biogas was conducted by the 'dry method' using bog iron ore. Biogas flowed through adsorbers filled with bog ore, where sulphur compounds were retained. At the same time, compressed air was supplied for the regeneration. The efficacy of the process depended on the capacity of ore, and clearly decreased when the amount of settled sulphur reached 25 % of the initial ore mass.

Table 1

'Hajdow' biogas composition [3]

Gas type	Percent volume [% vol.]
CH_4	65.0
CO_2	33.7
N_2	0.2
H_2S	1.1

During the last modernization, there was a change in the technology for the removal of hydrogen sulphide. The method of hydrogen sulphide removal in via a cylindrical bed. This is an economic and highly effective method of hydrogen sulphide removal from biogas currently used in WWTP. The process of biological removal of H_2S from biogas consists in its aeration to the form of simple sulphur or sulphate by bacteria. Sulphur bacteria engaged in this process develop inside the upper part of the reactor which is filled with polymer elements with an appropriately shaped surface, enabling the settling and development of bacteria. The layer consisting of special forms of Tiobacteria is located on the external surface of the carrier material. These bacteria use the process of H_2S aeration as a source of energy for development and prolification. Microbiological aeration results in the conversion of approximately 75 % of H_2S to simple sulfur, and to approximately 25 % of sulfates. Purified gas is transported to the tank.

Figure 5 presents the amount of production of biogas and the way of its management in 2013.

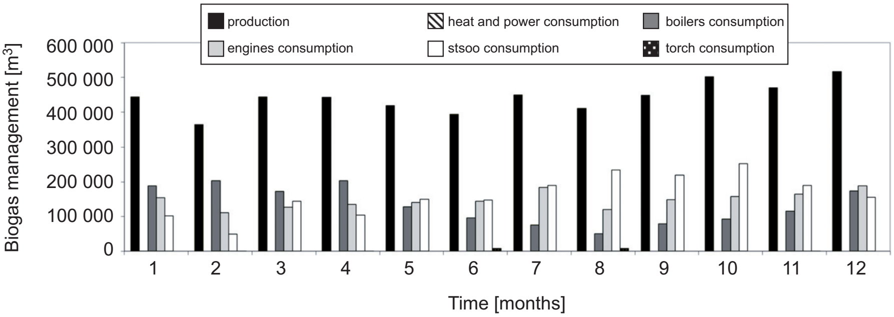

Fig. 5. Biogas management in 2013 [3]

Conclusions

The first modernization undertakings in the 'Hajdow' WWTP began soon after its construction, and have been constantly carried out until today, while further undertakings are planned. The need for modernization was caused by adjustment of Polish law to the EU Council Directive in the matter of urban waste and European standards specified in EEC/91/271. These requirements concern a decrease in the amount of contaminants – mainly biogenic compounds in purified sewage disposed to the receiver. Practically, from that time, modernization activities have been carried out in each part of the WWTP, mechanical, biological, and sludge processing. From the beginning of the functioning of the plant, many pieces of equipment and units have been modernized several times, eg rake bar screens, sand washers, and bioreactor chambers.

New investments covered the majority of units in the WWTP, which contributed to the decrease in the concentration of contaminants in the effluent from the plant, and improvement of the quality of water in the receiver – the Bystrzyca River.

The use of new solutions allowed an improvement in the effectiveness of the technological line in the plant.

As a result of the hermetic sealing of the elements with the greatest odour nuisance and application of biofilters, the noxiousness of the plant for both the local inhabitants and workers supervising the operation of the equipment, was reduced. This solution allowed avoidance of the creation of a costly protective zone around the plant.

After the completion of investments, the ‘Hajdow’ WWTP will belong to the group of the most modern and technologically advanced facilities of this type in Poland.

Acknowledgements

The authors express their thanks to the workers of the Municipal Water Supply and Sewage Systems, Co. Ltd. in Lublin, for making the necessary materials and data available, and assistance with writing this paper.

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WPŁYW MODERNIZACJI URZĄDZEŃ MIEJSKIEJ OCZYSZCZALNI ŚCIEKÓW „HAJDÓW" NA PRZEBIEG PROCESU OCZYSZCZANIA

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Abstrakt: W pracy przedstawiono wpływ modernizacji wybranych elementów ciągu technologicznego miejskiej oczyszczalni ścieków „Hajdów" na przebieg procesu oczyszczania ścieków. Autorzy zwrócili szczególną uwagę na zmiany w ilości powstających odpadów (skratki, piasek, osad nadmierny), spowodowane modernizacją, oraz na likwidację uciążliwości zapachowych oczyszczalni. Zmiany technologiczne w systemie bioreaktorów osadu czynnego przyczyniły się do znacznego wzrostu ilości osadu nadmiernego. Spowodowało to problemy z jego skutecznym zagospodarowaniem z użyciem stosowanych uprzednio metod i urządzeń, stąd też wprowadzono urządzenia wspomagające odwadnianie osadu nadmiernego. W związku z tym praca przedstawia również charakterystykę rozwiązań w zakresie przeróbki osadów wdrożonych dotychczas w oczyszczalni „Hajdów" oraz wprowadzane dalsze modernizacje.

Słowa kluczowe: osad czynny, gospodarka osadowa, uciążliwości zapachowe, biofiltry

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STATISTICAL APPROACH TO THE DETERMINATION OF THE INDEX OF SOIL SUPPLENESS ON REDUCTION

STATYSTYCZNE PODEJŚCIE DO OKREŚLANIA WSKAŹNIKA PODATNOŚCI GLEBY NA REDUKCJĘ

Abstract: The decrease in the redox potential in time can be determined on the basis of measurements in the aqueous soil suspension under standard laboratory conditions and time limits, as well as expressed as an index of soil suppleness on reduction (SSR index). Assuming that the SSR covers certain aspects of the relatively stable characteristics of the soil or soil properties, it can be practically considered as a useful indicator of the soil quality and fertility. The main aim of this study was to present a statistical method for determination of soil suppleness on reduction. The most practically useful statistical method to determine the soil susceptibility to reduction was the difference between the maximum and minimum Eh values obtained in the experiment. The Eh decrease values were within the range from 184 mV/week to 70 mV/week, while the soil suppleness on reduction index soil suppleness on reduction index (SSR index) for three soils tested was in the range from 25 to 10 mV/day. Results of statistical calculations and considerations upon the determination of soil suppleness on reduction index value based on the redox potential measurements in the soil-water suspension under laboratory conditions during a one week period, made it possible to significantly simplify the practical determination of the SSR index value.

Keywords: Eh measurements in soil, pH measurements, statistical calculations, soil suppleness on reduction index

Introduction

Phenomenon of the redox potential in soil refers to the soil solution and the extensive literature on redox potential studies in the soil was considered in different directions such as explaining the essence of the phenomenon of redox processes in the soil.

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Research upon the associations between different constants of soil properties and redox potential, identifying the relationships between variable soil conditions and redox potential, as well as a lot of attention was also paid to methodological aspects of redox potential measurements in the soil [1].

The redox potential (Eh) measurements actually show the current state of the redox potential in soil or in the soil-water medium and only at the time of measurement. However, measurements of redox potential in the aqueous suspension of soil under standard laboratory conditions and particular time limits, can be a base for determining the redox potential decrease over time and express it as an indicator of soil suppleness on reduction (SSR index). Assuming that SSR index covers certain aspects of the relatively stable characteristics of the soil, *ie* soil properties, it can be considered as practically useful indicator of soil quality and fertility [2]. The main aim of this study was to present statistical method for determination of soil suppleness on reduction index.

Methods

The research was conducted in the laboratory using three soil samples representatively collected from the topsoil of three arable fields near Lublin in 2012. Soil samples were dried under natural conditions and sieved through a plastic sieve with a diameter of 1 mm. The basic properties were determined in the soil samples. Distribution of soil particles was determined by means of Cassagrande's areometric method modified by Proszynski. Organic carbon was analyzed by Tiurin's method due to oxidation of soil organic matter in concentrated H_2SO_4. Total nitrogen was determined by Kjeldahl's method after digestion in concentrated H_2SO_4. The contents of extractable Fe and Mn were determined according to Rinkis after extraction with 1 mol HCl dm^{-3}, and the measurement of elements was performed by means of atomic absorption spectrometry applying Hitachi Z-8200 device. All chemical analyzes were performed in 4 replicates. The ratios of determined elements as molar ratios of elements were also calculated based on the amount of substance in the system of a given element to the subsequent one. The study included pH and redox potential measurements (Eh) and statistical experimental unit consisted of the soil suspension in a 100 cm^3 capacity beaker, prepared from 50 g of air-dried soil and 50 cm^3 of distilled water, *ie* at the soil to water ratio equaled to 1 : 1. Air temperature in the laboratory during measurements was about 25 ^{o}C. The pH measurements were made by means of potentiometer applying P-730 device provided with automatic temperature compensation and combined electrode ESAgP-30IW. Measured pH values were expressed as real values of pH and also as recalculated onto H^+ based on the dependence between pH and H^+, *ie* hydrogen ions concentration [3].

Redox potential measurements were made using P-730 device with the range of ±960 mV, and provided with platinum electrode of 5 mm length and 0.5 mm diameter, against calomel electrode EK-602. Polarization time of Pt electrode was 300 seconds. Eh values were calculated by adding to the value of redox potential, constant value of calomel electrode potential that for the conditions adopted in the experiment was +245 mV.

The pH and Eh measurements were carried out for three soils in 4 replicates and 8 terms of measurements, *ie* after 1 hour and then every 24 hours, *ie* after 1, 2, 3, 4, 5, 6, and 7 days of incubation; the whole experiment was repeated 5 times. Therefore, the experimental design consisted of 3 soils in 4 replicates for 8 measurement terms and in 5 replicates of the whole experiment. Thus the total number of experimental data of pH and Eh was $n = 480$.

Experimental data of the H^+ and Eh were calculated according to analysis of variance and *Tukey's-test*. Selected statistical characteristics were also calculated:

1. Arithmetic mean:

$$\bar{y} = \frac{\sum y}{n}.$$

2. Confidence interval $\bar{y} - L < \mu < \bar{y} + L$, where $\pm L$ is:

$$L = t_\alpha \sqrt{\frac{nS^2}{n(n-1)}},$$

where t_α is a value from t-Student's table *t-distributions* at the significance level of $\alpha = 0.05$, sum of squares:

$$nS^2 = \sum y^2 - \frac{\left(\sum y\right)^2}{n}$$

was calculated for the sample size of n, and degree of freedom $v = n - 1$.

3. Standard deviation $S = \sqrt{S^2}$ was calculated as the square root of variance:

$$S^2 = \frac{\sum y^2}{n} - (\bar{y})^2.$$

4. Standard error for mean value:

$$SE_{\bar{y}} = \frac{S}{\sqrt{n}}.$$

5. Minimum value *Min*.
6. Maximum value *Max*.
7. Range between maximum and minimum values *Range* = *Max* – *Min*.
8. Variance coefficient was calculated as a ratio of standard deviation to arithmetic mean $CV = S / \bar{y}$ expressed in %.
9. The linear regression equation $y = b_{yx} + c$ for selected measurement characteristics.
10. Determination coefficient R^2 [4].

Results

Soils in presented laboratory experiment were little diverse referring to their physical properties, although soils No. 1 and No. 3 were sandy loam, while soil No. 2 was silt loam. In contrast, soils were more diverse in terms of chemical properties such as pH, as well as the content of organic carbon, total nitrogen, and contents of extractable Fe and Mn. The characteristics of soils also shows the calculated ratios of determined elements as an additional feature of the soil chemical properties, *ie* ratios of elements calculated on a base of the significant and particular property of matter that is variable molecular weight of elements. Therefore, this method of calculating the molar ratios of elements may be considered as one and only correct way for calculating the ratios of chemical elements (Table 1).

Table 1

General properties of soils in the experiment

Feature	Soil		
	No. 1	No. 2	No. 3
Soil fraction and particle size [%]			
Sand ∅ 2–0.02 mm	66	71	74
Silt ∅ 0.02–0.002 mm	30	23	23
Clay ∅ < 0.002 mm	4	6	3
The pH index in 1 mol KCl pH [-]			
Value of pH	4.6	5.5	6.0
Element content [mg/kg]			
Organic-C	8585	7135	7773
Total-N	1876	1568	1764
Extractable-Fe	1386	792	853
Extractable-Mn	223	132	182
Elements ratio	Molar ratio [-]		
C/N	5	5	5
C/Fe	29	4	42
C/Mn	176	247	195
N/Fe	5	1	8
N/Mn	33	47	38
Fe/Mn	6	59	5

Biological processes associated with decreasing the oxygen content in the soil-water suspension increased the advantage of reduction processes, which can be represented as $Fe(OH)_3 + e^- \leftrightarrow Fe(OH)_2 + OH^-$. Table 2 presents ranges of the pH value, for which every range was represented by sample size of $n = 20$.

Table 2

Minimum and maximum values of the pH in the soil-water suspension during subsequent terms of measurement

Soil No.	Term of measurement							
	Hour 1	Day 1	Day 2	Day 3	Day 4	Day 5	Day 6	Day 7
	pH [-]							
1	4.67–5.08	4.99–5.35	5.18–5.74	5.37–5.79	5.46–5.97	5.52–5.97	5.72–6.09	5.72–6.15
2	5.71–6.28	6.08–6.40	6.14–6.64	6.26–6.64	6.37–6.60	6.37–6.63	6.48–6.73	6.48–6.75
3	6.16–6.84	6.48–6.84	6.58–7.00	6.65–7.00	6.79–6.97	6.79–6.99	6.83–7.03	6.84–7.10

Oscillations of pH values were slightly variable in subsequent measurement terms, and during the whole experiment, differences between the ranges for soils and terms were significant, although values of the pH ranges varied with a clear tendency of pH

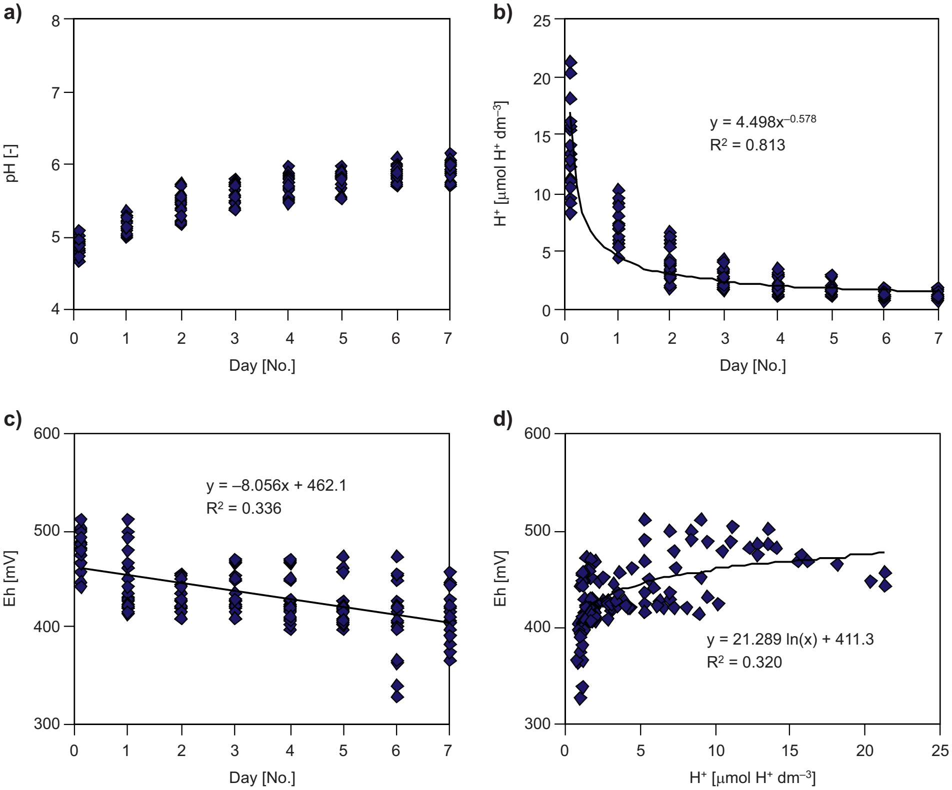

Fig. 1. Dependencies and associations among examined measurement features in soil-water suspension for the soil No. 1 at the sample size *n* = 160; a) Dependence between measurement term in days and pH index, b) Relationship between measurement term in days and H^+ ions concentration, c) Relationship between measurement term in days and Eh values, d) Relationship between H^+ ions concentration and Eh values

increase, which was illustrated for three tested soils in Fig. 1a, Fig. 2a, and Fig. 3a. Quantitative representation of the decreasing the hydrogen ions concentration H^+ and possibility of calculating the *f*(*x*) was presented in Fig. 1b, Fig. 2b, and Fig. 3b, where relatively wide range of H^+ in three experimental soils can be seen. Associations between pH values and Eh values can be also compared in Fig. 4 for soils No. 1, No. 2, and No. 3 as well as calculated data for the relationship *f*(*x*) between H^+ concentration and Eh values in Fig. 1d, Fig. 2d, and Fig. 3d. These graphs show that such features as pH and Eh may be compared and present altogether, while calculation of *f*(*x*) may be performed only when the pH values are converted into the hydrogen ions concentration H^+. Ranges of the pH values presented in Table 2 also indicate data such as pH cannot be statistically calculated. The explanation would be three theses presented without proving them. First: pH 4 is not 4, and pH 8 is not 8. Second: mean for pH 5 and pH 7 is not pH 6. And third: difference between pH 5 and pH 6 is not pH 1. Anyone can easily verify by reviewing the scientific literature in serious and well-known scientific journals that statistical calculations using pH are simply very often incorrect [5].

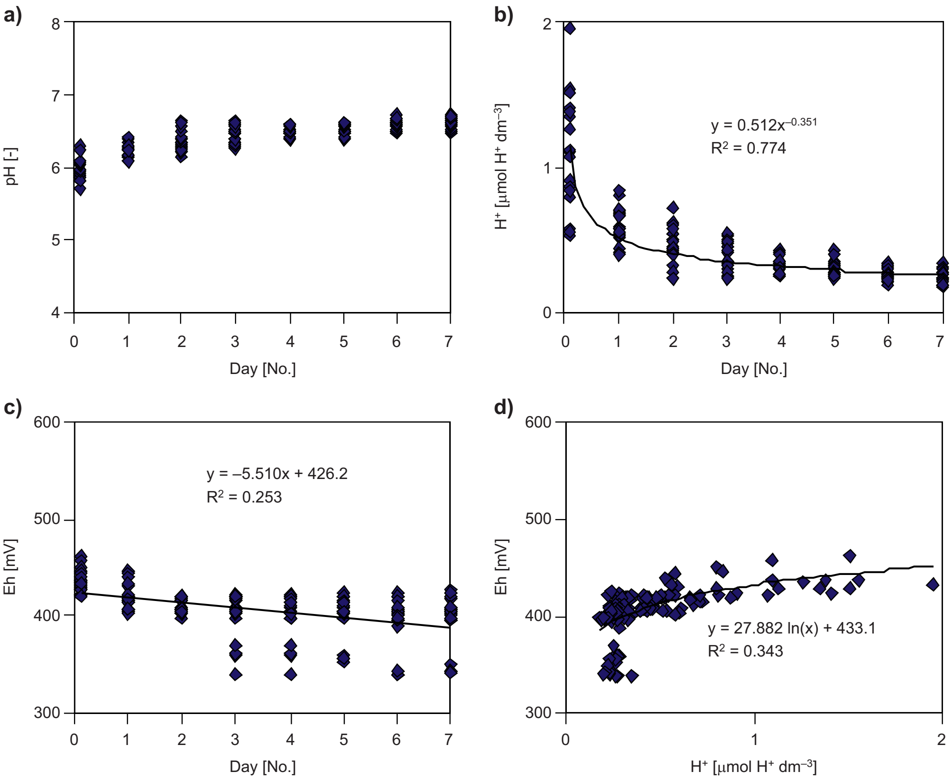

Fig. 2. Dependencies and associations among examined measurement features in soil-water suspension for the soil No. 2 at the sample size *n* = 160, a) Dependence between measurement term in days and pH index, b) Relationship between measurement term in days and H^+ ions concentration, c) Relationship between measurement term in days and Eh values, d) Relationship between H^+ ions concentration and Eh values

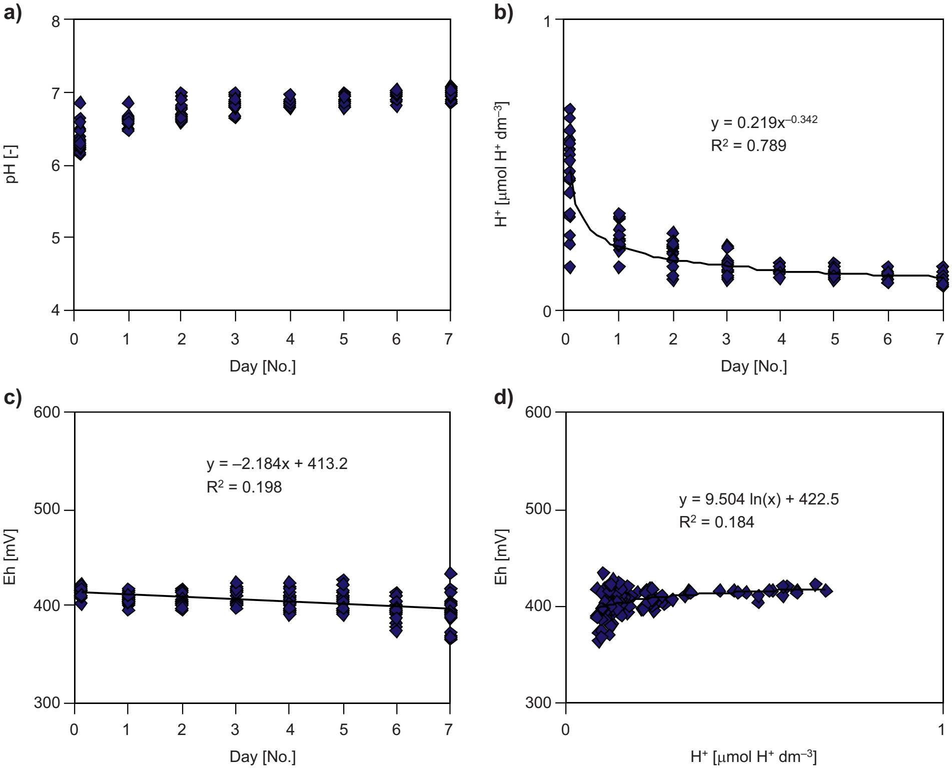

Fig. 3. Dependencies and associations among examined measurement features in soil-water suspension for the soil No. 3 at the sample size n = 160, a) Dependence between measurement term in days and pH index, b) Relationship between measurement term in days and H^+ ions concentration, c) Relationship between measurement term in days and Eh values, d) Relationship between H^+ ions concentration and Eh values

Table 3 presents the H^+ concentration in soil-water suspension under the influence of experimental treatments.

Table 3

Concentration of the H^+ ions in the soil-water suspension during subsequent terms of measurement

Soil	Term of measurement								Mean
	Hour 1	Day 1	Day 2	Day 3	Day 4	Day 5	Day 6	Day 7	
	H^+ [μmol H^+ dm^{-3}] for sample size $n = 480$								
No. 1	13.8032	6.8614	4.0537	2.7692	2.0878	1.7136	1.3830	1.2322	4.2380
No. 2	1.1090	0.6070	0.4573	0.3747	0.3171	0.2938	0.2564	0.2390	0.4568
No. 3	0.4758	0.2515	0.1949	0.1537	0.1394	0.1305	0.1120	0.1000	0.1952
Mean	5.1293	2.5733	1.5686	1.0992	0.8481	0.7126	0.5838	0.5237	1.6298
LSD at p = 0.01, for soils 0.2617, for terms 0.5538, for soil × term 1.1202									

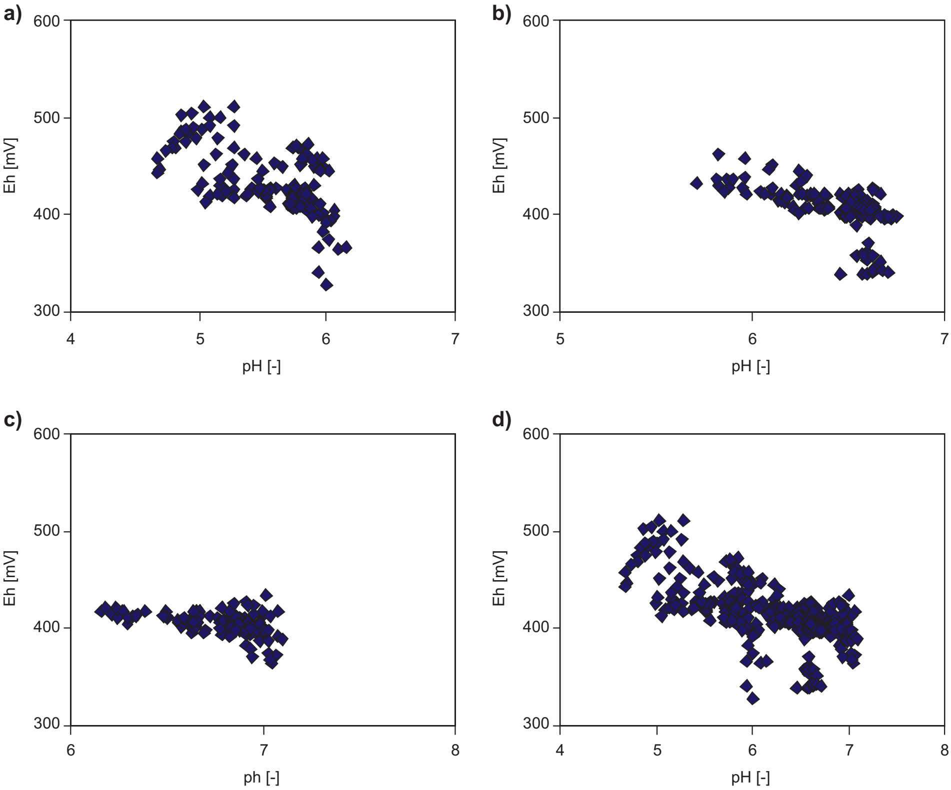

Fig. 4. Dependencies between pH and Eh values in soil-water suspension for examined soils and sample size *n* = 160: a) No. 1, b) No. 2, c) No. 3 as well as d) for three soils (No. 1, No. 2 and No. 3 altogether) and sample size *n* = 480

Values of hydrogen ions concentration H^+ were significantly varied especially between soils No. 1 and No. 2, and in majority the H^+ values were also significantly diversified between soils No. 2 and No. 3. Considerable differences between measurement terms occurred just after several days of incubation. The results for H^+ can be also recalculated onto pH, but such presenting of pH values would, however, be only of the demonstration importance with a very clear stipulation, that the calculated value of the least significant difference (LSD) expressed in the concentration of hydrogen ions H^+ cannot ever be converted into the pH value, because it would be completely incorrect.

Table 4 presents statistically calculated Eh values for 3 soils and 8 measurement terms. The highest significant mean Eh value was found for soil No. 1, while no significant differences were recorded between mean values for soils No. 2 and No. 3. There were significant differences between mean values of Eh in the subsequent measurement terms, but most of them were observed rather in the initial measurement terms and a few days intervals; these differences were smaller in the final terms of measurement. It can be also assumed that the least significant difference for the interaction of soil × term of 22.5 mV, can be the Eh value indicate for a significant difference for each mean of Eh values in the soil-water suspension, but with the restriction that this value is characteristic only for this experiment.

Table 4

The Eh values in soil-water suspension during subsequent terms of measurement along with statistical characteristics

Soil	Term of measurement								Mean for soil
	Hour 1	Day 1	Day 2	Day 3	Day 4	Day 5	Day 6	Day 7	
	Eh [mV] for sample size $n = 480$								
No. 1	470.7	455.3	429.7	434.0	428.7	427.6	411.6	411.9	433.7
No. 2	435.9	419.6	411.4	403.0	398.0	398.8	393.1	399.4	407.4
No. 3	414.5	407.4	405.9	409.4	405.9	407.2	398.4	394.7	405.4
Mean	440.4	427.5	415.7	415.5	410.8	411.2	401.0	402.0	415.5
LSD at p = 0.01, for soils 5.2, for terms 11.1, for soil × term 22.5									

The list of Eh values in Table 4 best illustrates the average dynamics of the redox potential decrease both for soils and measurement terms. Nevertheless, calculated statistical characteristics for the soils are appropriate statistical evaluation of all Eh measurements in soil-water suspension during the incubation (Table 5).

Table 5

Statistical characteristics of the Eh values in soil-water suspension for experimental soils

Statistics	Soil		
	No. 1	No. 2	No. 3
	Eh [mV] for sample size $n = 160$		
Mean for soil*	433.7	407.4	405.4
Confidence interval	± 4.9	± 3.9	± 1.7
Standard deviation	31.7	24.9	11.2
Standard error	2.5	2.0	0.9
Minimum	327.6	339.2	364.6
Maximum	511.7	462.2	434.2
Range	184.1	123.0	69.6
Coefficient of variation	7 %	6 %	3 %

* See Table 4.

Under natural circumstances of the soil environment, *ie* in the system with dynamic air-water conditions, redox potential measurements can be performed, but the soil must be moist in order to the measurement to be possible. In the soils moisturized with water, the redox potential values change rapidly and reach values indicating the current state of oxygenation or reduction. However, in the simulated soil solution at a predetermined ratio of soil to water, reducing conditions at the level of 332 mV can be achieved after several days of incubation at a specific temperature [6]. The decrease of redox potential values in the period, e.g. one week, may be an index of soil susceptibility on reduction as a important indicator for physical, chemical, and biological soil properties. To simplify the determination of such SSR index, only two series of measurements Eh should be conducted. The first, one hour after preparation of the soil-water suspension, and the second measurement after 7 days, *ie* one week of incubation. Of course, the pH measurement could be some additional characteristics of the soil. However, a research should be made at first to be able to develop an interpretation of these Eh and pH measurements.

All the results from chemical analyzes and measurements are more or less variable, which is related to methods, apparatus, and conditions, hence all analytical data should be statistically processed [7]. Redox potential measurements, even in a relatively homogeneous environment such as soil and water suspension, are so variable that a statistical processing of Eh values is actually necessary. Table 5 presents eight important statistical characteristics referring to Eh values achieved during the whole experiment (Table 4). Among statistical measures listed in Table 5, two groups can be distinguished. The first consists of the position measures: arithmetic mean, confidence interval, and standard deviation. Second includes the variability measures: standard deviation and variability coefficient. The only relative measure among all statistical characteristics is variability coefficient that is suitable for comparisons of variability of features expressed in different units.

Table 6 illustrates statistical characteristics of Eh values that can be a basis for determination of the soil suppleness on reduction index.

Table 6

Methods for determining the soil suppleness on reduction index based on statistical characteristics

Statistical way	Soil			Mean
	No. 1	No. 2	No. 3	
	Decline of the Eh [mV] per week			
First and last*	58.8	36.5	19.7	38.3
Range**	184.1	123.0	69.6	125.6
Coefficient b_{yx}***	8.0	5.5	2.1	5.2
Mean	83.6	55.0	30.5	56.4

* Difference between the first and last mean Eh value for measurement terms, see Table 4; ** Range as the difference between maximum and minimum of Eh value for all measurements, see Table 5; *** Value of regression coefficient b_{yx} for linear equation $y = b_{yx} + c$ describing Eh features and measurement terms, see Fig. 1c, Fig. 2c, Fig. 3c.

First: 'First and last', *ie* the difference between the first and the last mean Eh value measured for terms from Table 4. Second: 'Range', *ie* the difference between maximum and minimum values of Eh for all redox potential measurements in soil-water suspension during a one week. Third: 'Coefficient b_{yx}', *ie* value of regression coefficient b_{yx} from the linear equation describing Eh values and measurement terms. Comparison of the average decline in the redox potential values for the three approaches to determine the soil suppleness on reduction shows good agreement of the trend for all soils (Table 6).

In general, the largest values of redox potential decrease were recorded in soil No. 1, smaller in soil No. 2, while the smallest in soil No. 3 for all three ways. The lowest values of the redox potential decrease were observed for the soil suppleness on reduction determined on a base of the regression coefficient b_{yx}. Higher values occurred for the process of determining the difference from the first and last average Eh value for the measurement terms. Therefore, it can be assumed that both the 'First and Last', and 'Coefficient b_{yx}' methods are not useful to determine the soil suppleness on reduction index. 'Range', as the difference between maximum and minimum Eh values obtained during the experiment, was the most practically useful statistical way to determine the soil suppleness on reduction. Approximate value of Eh decrease for soil No. 1 was 184 mV/week, for soil No. 2 was 123 mV/week, and for soil No. 3 was 70 mV/week. Therefore, the SSR index for soil No. 1 was expressed in a decrease of 25 mV/24, for soil No. 2 the drop was 18 mV/24 hours, and for soil No. 3 this fall amounted to 10 mV/24 hours.

The results in Table 1 and Table 6 may suggest – because it was not a subject of the research – that the sequence of soil suppleness on reduction for the experimental soils lines up as follows: No. 1 > No. 2 > No. 3, which means that soil No. 1 is characterized by the highest susceptibility to reduction and in addition, this soil contained the highest quantities of organic carbon, total nitrogen, as well as extractable Fe and Mn. It may also indicate that the soil suppleness on reduction index may be compatible with chemical properties of the soil, which would give a greater chance to accept the SSR ratio as one of many important indicators of soil properties.

Figure 4 shows the dependence between the values of pH and Eh for soils used in the experiment, and the overall dependence between pH and Eh for 3 soil altogether. The Eh value ranges are different in reference to Eh scatter, although they cover a similar range for the three experimental soils between 300 and 500 mV. Due to the comparison of examined dependences between pH and Eh, such dependencies cannot be calculated statistically, but of course they can be graphically assembled to be able to see how these dependencies run. Thus, the pH ranges in soil No. 1 were mainly from pH 4.5 to pH 6, in soil No. 2 from pH 5.5 to pH 7, and in soil No. 3 from pH 6 to pH 7, *ie* from pH 4.5 to pH 7 for a total of three soils examined. Dependencies between pH and Eh described in literature conclude that with the silent assumption this value is –59 mV/pH [8], meanwhile, such value of decline in the redox potential expressed in mV, when the pH changes by 'unity' between of two pH values, what from a statistical point of view is incorrect.

And here, a simple theory without any evidence may be announced: the concentration of hydrogen ions in the solution expressed in mol H^+ dm^{-3} for the range between pH 4 to pH 5, are completely different values the H^+ than in the range between pH 5 to pH 6, and further than in the range from pH 6 to pH 7, as well as than from pH 7 to pH 8, and thus for subsequent intervals between pH values, there are indeed different the H^+ values for each 'space' between certain values of pH index [6].

Conclusions

Presented results of statistical calculations and considerations upon determination of the soil suppleness on reduction index based on measurements of redox potential the soil-water suspension under laboratory conditions during a period of one week, made it possible to significantly simplify the practical determination of the SSR index.

Practically, it is possible on the basis of only two series of independents of Eh measurements in soil suspension, *ie* the first: the five Eh measurements after one hour of incubation, and the second: the five Eh measurements in the same soil suspension after 7 days of incubation.

Determination of the range between the maximum and minimum values for all redox potential measurements in soil-water suspensions, can be accept as a good enough way of determining the index of soil suppleness on reduction in laboratory conditions.

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STATYSTYCZNE PODEJŚCIE DO OKREŚLANIA WSKAŹNIKA PODATNOŚCI GLEBY NA REDUKCJĘ

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Abstrakt: Na podstawie pomiarów potencjału redoks w wodnej zawiesinie glebowej w standardowych warunkach laboratoryjnych i określonych terminach pomiarów można określić spadek wartości potencjału redoks w czasie i wyrazić to jako wskaźnik podatność gleby na redukcję (SSR index). Przyjmując, że wskaźnik podatności gleby na redukcję obejmuje pewne aspekty względnie stałych cech glebowych, czyli właściwości gleby to możne być rozważany jako praktycznie przydatny wskaźnik jakości i żyzności gleby. Głównym celem pracy było zaprezentowanie statystycznego sposobu wyznaczania wskaźnika podatności gleby na redukcję. Najbardziej praktycznie przydatny statystyczny sposób do określania podatności gleby na redukcję to była różnica między maksymalnymi a minimalnymi wartościami Eh uzyskanymi w doświadczeniu. Wartości spadku Eh były w przedziale od 184 mV/tydzień do 70 mV/tydzień. A wskaźnik podatności gleby na redukcję SSR index dla trzech gleb testowanych był w przedziale od 25 do 10 mV/dobę. Przedstawione wyniki obliczeń statystycznych i rozważań nad określeniem wartości wskaźnika podatności gleby na redukcję na bazie pomiarów potencjału redoks w zawiesie gleba–woda w warunkach laboratoryjnych w okresie jednego tygodnia, dały możliwość znacznego uproszczenia praktycznego określania wartości wskaźnika podatności gleby na redukcję (SSR index).

Słowa kluczowe: pomiary Eh w glebie, pomiary pH, obliczenia statystyczne, wskaźnik podatności gleby na redukcję

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INVASIVENESS AND REPRODUCTION OF THE *Steinernema feltiae* FROM SELECTED AGROCOENOSE LOCATED IN WIELUN

INWAZYJNOŚĆ I ROZRODCZOŚĆ *Steinernema feltiae* Z WYBRANEJ AGROCENOZY WIELUNIA

Abstract: Faunistic studies to find the presence of nematodes of the family *Steinernematidae* were performed. Soil samples were collected from pasture area located in the municipality of Wielun (Lodz Province). Latitude and longitude of the sampling site was determined with the Gnomon software. Physico-chemical properties of samples were analyzed in the Analytical Centre of the Warsaw Agricultural University. Total lead content was analyzed with the flame atomic absorption spectrophotometry and soil pH – potentiometrically. Nematodes were isolated from the soil samples in the laboratory conditions, using method described by Bedding and Akhurst in 1975. *S. feltiae* (Filipjev 1934) were determined using the key for the determination of the species (Lacey 1997) and by molecular analysis. It was shown that nematodes from the investigated area were characterized by higher biological activity (the intensity of the invasion, the degree of migration) and longer duration of development (time of killing the host and the time needed to start migration), in comparison with nematodes from commercial biopreparation.

Keywords: entomopathogenic nematodes, *Steinernema feltiae, Galleria mellonella*

Entomopathogenic nematodes of the families *Steinernematidae* and *Heterorhabditidae* are used in biological plant protection. The animals are closely associated with bacteria of the genera *Xenorhabdus* sp. and *Photorhabdus* sp. The nematodes are characterized by a great fertility and a broad host spectrum [1–3]. Invasive larvae of the animals, under optimum conditions, are able to persist in soil and to actively search, infect and kill the insect host. They are now massively reproduced on artificial media and processed to produce bioinsecticides [4, 5].

Entomopathogenic nematodes occurring in the soil often are exposed to natural environmental resistance limiting their biological activity. The ability of the invasion of nematodes and their effectiveness in reducing insect populations is influenced by many biotic and abiotic factors [6, 7].

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Important abiotic factors are: soil structure, soil pH and heavy metals. An example is the lead (II), whose harmful effects on entomopathogenic nematodes proven in many studies [8–10]. Both lead and nematodes gather in the upper soil layers. Lead accumulates there and is not washed out downwards. Therefore, its harmful impact may last for years [11].

On the biological activity of nematodes also influences soil pH [12]. Optimum soil pH for many soil organisms is in the range 5.5–7.2 [13]. Research has shown that low soil pH a negative effect on survival and invasive larvae of nematodes [12, 14].

Soil structure also can have a big impact on entomopathogenic nematodes. In sandy substrates, and sand-clay recorded the highest survival and activity of these animals [7].

Scientific data suggest that the selection of indigenous breeds of nematodes is more beneficial than the use of commercial preparations based on nematodes. Such investigations are carried out in many countries around the world, including Hungary [15]. In Poland, however, lack of detailed studies of biogeographical data, a collection of useful species and breeds entomopathogenic nematodes effectively limiting the populations of harmful insects.

The aim of this study was to analyze insecticidal properties of nematodes isolated from natural environment in comparison with those from commercial biopreparation.

Materials and methods

Acquirement of samples from environment. Studies were carried out in the summer season of the years 2010–2011. Fifty soil samples were taken with the Egner's sampler from a soil layer 0–25 cm in selected study area (natural meadows) located in the municipality of Wielun (Lodz Province). The method ensures complete and even sampling which allows obtaining the actual spatial distribution of environmental pollution by lead and of nematode densities in the soil.

Latitude ($51^{o}14'24''$) and longitude ($18^{o}40'36''$) the geographical position of the species was determined with the Gnomon 3.3. software.

Soil samples, were examined in terms of physico-chemical industries in Analytical Center SGGW. Total lead content in soils was determined by flame atomic absorption spectrometry (FAAS) and soil pH was determined by potentiometry [16, 17].

For the studies caterpillars of greater wax moth (*Galleria mellonella* L.) with an average body weight of 187 mg were used as a host. Larvae of entomopathogenic nematodes *Steinernema feltiae* investigated in this study were taken from the soil samples in the laboratory by insect trap method (Bedding and Akhurst) [18]. Well mixed soil samples were placed in plastic boxes of a volume of 250 cm^3 together with two trap insects (caterpillars of *Galleria mellonella* L.). Samples were then placed in the POL-EKO ST1 incubator at temperatures 20 ^{o}C for 16 days. Every second day, dead insects were isolated and replaced with fresh living ones. Infected larvae were placed on the migratory sponges and stored at temperature of 20 ^{o}C for the time necessary to obtain nematode larvae. Once nematodes left the host cavity, they were regularly picked up to tissue culture bottles and stored at 4 ^{o}C. Nematode species was determined using the key to the determination [19] and by molecular analysis (sequencing of the PCR product with primers complementary to the ribosomal RNA genes of *S. feltiae*).

Genetical analysis. Total DNA from pure culture of some isolations of selected nematodes were purified using Genomic mini column kit (A&A Biotechnology). Purified DNA isolates were analyzed via gel electrophoresis in 1 % agarose, Than DNA were used as a template in PCR with primers SF18SL and SF18SR designed by author and synthesized in Institute of Biochemistry and Biophysics PAS. Primers allow to amplify fragment started at the terminal part of 18S rRNA gene and contains ITS1 region, 5.8S RNA gene, ITS 2 region and finished at the beginning part of 23S rRNA gene. Sequences of primers are presented in Table 1.

Table 1

Primers used in PCR with *S. feltiae* DNA

Name	Sequence
SF18SL	GTACACACCGCCCGTCGCTGC
SF18SR	AAATCCTAGTTAGTTTCTTTTCCTCCGC

PCR reactions were performed in 0.2 cm^3 tube. For each reaction 22 mm^3 of PCR MasterMix (A&A Biotechnology) supplemented with both primers (each concentration 0.2 μM) was mixed with 10 mm^3 of nematode DNA template and finally 18 mm^3 of ultrapure water was added. Mastercycler PRO (Eppendorf) was used for PCR. Condition of PCR is presented in Table 2.

Table 2

PCR condition for *S. feltiae* analysis

Phase	Temperature [^{o}C]	Time [min]	No. of cycles
Initial denaturation	94	3	1
Denaturation	94	0.5	35
Annealing	66	0.5	35
Extension	72	0.5	35
Final extension	72	5	1

Small piece of PCR products (10 mm^3) were analyzed by electrophoresis in 1 % agarose gel. Than the rest of products were purified using Clean-Up kit (A&A Biotechnology) and sequenced (CoreLab of Medical University in Lodz).

Analysis of sequences was performed using BioEdit 5.0.6. software. For alignment ClustalX 2.012 [20] was used.

S. feltiae from a biological preparation “Owinema” were used as a control.

Insecticidal property analysis. The experiments were performed in Petri dishes in the POL-EKO ST1 incubator at 20 ^{o}C. For infection of insect the dose of 50 infective juveniles (IJs) nematodes per insect were used. It was the optimal dose to obtain the maximum number of larvae of nematodes [21]. The same doses were used to investigate the mortality of insects, extensiveness and intensity of invasion. Dead insects were dissected two days after their death.

In the experiment, the about 400 caterpillars of *G. mellonella* were applied. There were used to isolation of nematodes from soil samples (200 caterpillars), for dissection during analysis of the intensity of the invasion (150 caterpillars) and for the analysis of nematode reproduction (50 caterpillars). This parameter was tested during five consecutive days after the first appearance invasive larvae in an artificial environment outside (Petri dish). Total number of larvae that managed to leave the host body for the day and the number of live larvae (capable of following an invasion) was assessed.

For the statistical analysis used analysis of variance of one variable (UNIANOVA). The experiment was repeated twice.

Results and discussion

The analysis of physico-chemical soil samples showed a natural content of lead (II) (6.86 ppm) and acidic (5.62). Granulometric soil subgroup was defined as sandy clay. Above parameters are characteristic for the environments appropriate to the occurrence of entomopathogenic nematodes. This is also acknowledgement by the results received of other researchers [7, 8, 14].

In the analyzed soil samples found to larvae of entomopathogenic nematodes and morphometric measurements of all development stages of nematodes and comparison with the key shown that the analyzed nematodes belonged to species *S. feltiae*. The obtained results were also confirmed using the PCR reaction. Species caught in one of the largest populations of nematodes occurring in Polish [6, 22].

During analysis of the biological activity of nematodes has been shown that the total mortality insects, nematodes infecting subjects from habitat, remained at the same level as a control (nematodes from biopreparation). Extensiveness of invasion was slightly low compared with the control sample, but this result still indicates a high efficiency of occurring naturally in the habitat nematodes against insects (Table 3).

Table 3

The biological activity of *S. feltiae*

Tested samples	Control	Nematodes from investigated areas
Total mortality of insects [%]	100	100
Extensiveness of invasion [%]	100	98
Intensity of invasion [pcs.]	8^a	9^b
Time to kill the insect by the nematode [days]	2	4
The first day of the migration of invasive larvae from the insect-host to the external environment [days]	8	18

Different letters in columns denote significant differences at $p < 0.05$.

The intensity of the invasion of isolated from the habitat nematodes was a slightly higher than the control sample, and conducted analysis of variance shown important differences between the control sample, and nematodes from land (Table 4).

Table 4

Variance analysis for "invasion intensity" feature

Source of variation	Type III sum of squares	df	Mean square	F	Significance
Model adjusted	1679(a)	1	167	14	$p < 0.001$
Constant	17888	1	17888	1477	$p < 0.001$
Habitat	167	1	167	14	$p < 0.001$
Error	2883	238	12		
Total	20938	240			
Total adjusted	3050	239			

(a) – R square = 0.055 (corrected R square = 0.051).

Examining the time of death caterpillars after infection nematode (time of killing an insect – host) was in the sample of nematodes from the habitat the municipality Wielun, longer than control sample (Table 3). This time is also much more than gives other researchers [21].

A similar relationship was recorded by analyzing the time required to start the migration invasive larvae of the host body to the external environment. The first day on which the presence of larvae was observed in the external environment, have been reported at 18 days of infection, whereas for the control of nematodes to migrate there have been at day 8 of insect infestation (Table 3).

Insect killing time and time of migration may indicate that entomopathogenic nematodes are food selectivity.

During analysis of the reproduction of nematodes from the habitat and the survival of their larvae after migration, has been observed that the number of alive larvae which emerged from the host's body is higher than in the population of nematodes in the control sample (Table 5, Fig. 1).

Table 5

Nematodes migration in the first and next successive four days with specification of the number of alive larvae [pcs.]

Days	Number of migration larvae from an insect [pcs.]			
	Control		Nematodes from investigated areas	
	Altogether	Alive	Altogether	Alive
1	3829	3829	23917	23483
2	12886	11517	19286	18979
3	21795	19251	13951	13559
4	13403	12756	10167	10052
5	12096	11586	11932	11532
Total	64009	58940[a]	79254	77605[b]

Different letters in columns denote significant differences at $p < 0.01$.

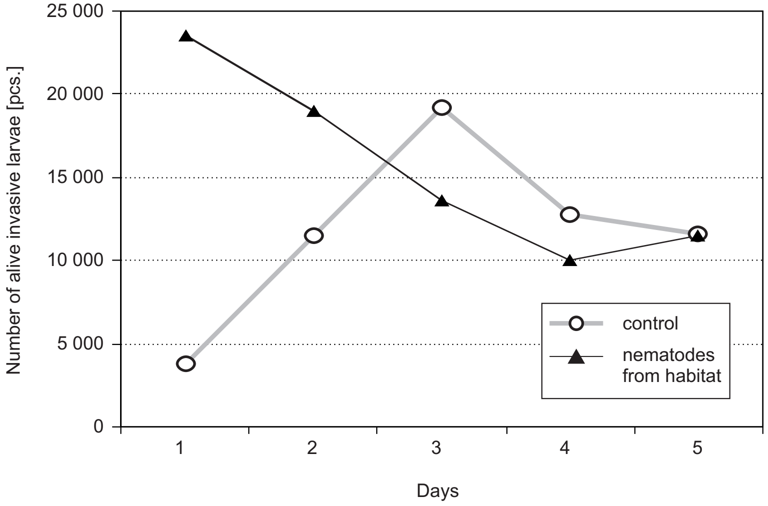

Fig. 1. Number of the alive invasive larvae of nematodes after migration

Mortality of larvae of nematodes from the area during the first five days of migration was lower compared with the control sample and was characterized by less dynamic than the mortality of larvae of nematodes from biopreparation (Table 5, Fig. 2).

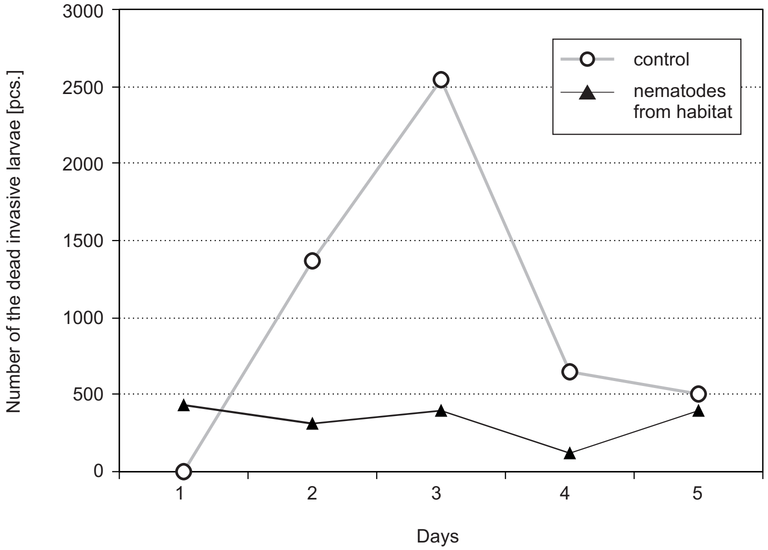

Fig. 2. Number of the dead invasive larvae of nematodes after migration

Statistical analysis of the invasive larvae, staying alive after migration from the host's body, showed the high essential difference between the number of investigated nematodes, and of the control sample (Table 6).

Table 6

Variance analysis for "nematodes reproductivity" feature

Source of variation	Type III sum of squares	df	Mean square	F	Significance
Model adjusted	712 663 381(a)	1	712 663 381	7 777	$p < 0.001$
Constant	37 407 552 526	1	37 407 552 526	408 227	$p < 0.001$
Habitat	712 663 381	1	712 663 381	7 777	$p < 0.001$
Error	549 806	6	91 634		
Total	38 120 765 713	8			
Total adjusted	713 213 187	7			

(a) – R square = 0.999 (corrected R square = 0.999).

Researches on the biological activity of nematodes from the habitat are still under development. It was shown that one of the most effective pathogens against pests (*eg* grubs of cockchafer) is entomopathogenic nematodes isolated from the habitat [23].

Results obtained also show that the nematodes originating from the habitat, characterized by higher reproduction and survival of invasive larvae than nematodes from biopreparation. Is important to continue and extend the research topic, which in future will enable better use of biological methods of plant protection.

Conclusions

1. Strains of nematodes isolated from the natural environment are characterized by higher biological activity (intensiveness of invasion, degree migration) than nematodes from biopreparation.
2. Development time (killing the host and the time required to migration) of nematodes isolated from natural environment is longer in comparison with nematodes from biopreparation.

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INWAZYJNOŚĆ I ROZRODCZOŚĆ *Steinernema feltiae* Z WYBRANEJ AGROCENOZY WIELUNIA

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Abstrakt: Przeprowadzono badania faunistyczne w celu stwierdzenia obecności nicieni z rodziny *Steinernematidae*. Próby glebowe pobrano z terenu użytku zielonego położonego w gminie Wieluń (województwo łódzkie). Długość i szerokość geograficzną stanowiska występowania gatunku oznaczono za pomocą programu komputerowego Gnomon. Próby zostały zbadane pod względem fizykochemicznym w Centrum Analitycznym SGGW. Oznaczono całkowitą zawartość ołowiu w glebie metodą płomieniowej absorpcyjnej spektrometrii atomowej (FAAS) oraz odczyn gleby metodą potencjometryczną. Nicienie wyizolowano z prób glebowych w warunkach laboratoryjnych, metodą Beddinga i Akhursta (1975). *S. feltiae* (Filipjev 1934) oznaczono przy pomocy klucza do oznaczania gatunku (Lacey 1997) oraz za pomocą analiz molekularnych. Wykazano, że nicienie pochodzące z badanego terenu charakteryzują się większą aktywnością biologiczną (intensywność inwazji, stopień migracji) oraz dłuższym czasem rozwoju (czas uśmiercenia żywiciela i czas niezbędny do rozpoczęcia migracji) w porównaniu z nicieniami pochodzącymi z komercyjnego biopreparatu.

Słowa kluczowe: nicienie entomopatogeniczne, *Steinernema feltiae*, *Galleria mellonella*

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CONTENT OF NICKEL IN MAIZE AND SOIL FERTILIZED WITH ORGANIC MATERIALS DERIVED FROM WASTE

ZAWARTOŚĆ NIKLU W KUKURYDZY I GLEBIE NAWOŻONEJ MATERIAŁAMI ORGANICZNYMI POCHODZENIA ODPADOWEGO

Abstract: The research was conducted to determine the influence of fertilization with waste organic materials on the content and uptake of nickel by maize as well as on the total nickel content in soil. The three-year field experiment comprised 7 treatments: a non-fertilized soil (control treatment) and a soil fertilized with mineral fertilizers, cattle manure, green waste compost, sewage sludge, compost from sewage sludge and straw as well as with a mixture of sewage sludge and hard coal ash. The content of nickel in the above-ground parts of plants and in the soil was determined using ICP-AES method.

During the research no nickel pollution of the plants and soil was found. A significant increase in the element content in maize as a result of fertilization was found only in the 2nd year of the research, after fertilization with mineral fertilizers. In the 1st year, the plants fertilized with the compost from sludge and straw, and in the 3rd year all the fertilized plants contained significantly less nickel than the control plants. Maize fertilized with the mixture of sludge and ash had the highest mean weighted nickel content. The total nickel uptake from the fertilized soil was higher than the uptake from the control soil. The soil fertilized with the green waste compost and the soil fertilized with the mixture of sludge and ash contained significantly more nickel than the non-fertilized soil.

Keywords: waste organic materials, sewage sludge, compost, nickel, trace elements

Physiological role of nickel is connected with, among other things, its occurrence in hydrogenases and in urease [1, 2]. Since nickel is indispensable for proper functioning of urease (an enzyme which breaks down urea to ammonia and carbon dioxide), an adequate supply of nickel is important during soil fertilization with urea. Follmer [3] draws attention also to the participation of urease in the processes of defense against phytopathogens. Moreover, nickel also plays a role in the processes of iron uptake and

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atmospheric nitrogen fixation [2]. Growth inhibition and leaf necrosis are symptoms of nickel deficiency [1, 2]. In animals and humans, nickel deficiency results in a decrease in the level of hemoglobin in blood, disorders in functions of the epidermis and in pigmentation, impairment of liver functions [4].

In the case of living organisms, not only deficiency of trace elements is harmful, but also their excess. Excess of nickel leads to chlorosis (caused by disordered iron uptake), it also causes disturbance in the course of the processes of atmospheric nitrogen fixation, photosynthesis, transpiration [4]. In animals and humans, exposure to nickel can be a cause of allergy; mutagenic and carcinogenic effects of nickel have also been found. The danger of environmental pollution with trace elements occurs, among other things, during fertilization with organic materials derived from waste.

The research was conducted to determine the influence of fertilization with waste organic materials on the content and uptake of nickel by maize as well as on the total nickel content in soil.

Material and methods

The 3-year field experiment was set up in 2008 at an experimental station of the University of Agriculture in Krakow and was continued in the next two years. The experiment was conducted on brown soil, with graining of light soil. It was an acid soil (pH_{KCl} = 5.40), which had a very high content of available phosphorus and potassium (94.9 mgP and 219.2 mgK $\cdot$ kg^{-1} d.m.). The soil contained 9.88 $gC_{organic} \cdot kg^{-1}$ d.m., 1.07 $gN_{total} \cdot kg^{-1}$ d.m., and 5.00 $mgNi_{total} \cdot kg^{-1}$ d.m. The content of trace elements in the soil did not exceed the limit values established for agricultural use of sewage sludge, neither did the pH_{H2O} value of the soil make fertilization with sewage sludge impossible – this applies to the values which were in effect during the field experiment [5, 6] and the values which are in effect now [7].

The experiment comprised 7 treatments: a non-fertilized soil (control) as well as a soil fertilized with mineral fertilizers, cattle manure, green waste compost, municipal sewage sludge, compost from sewage sludge and straw as well as with a mixture of sewage sludge and ash. Each treatment was carried out in 4 replications. Pioneer maize PR 39F58 was the test plant in all years of the research and it was grown for silage. In the first year, 160 kgN, 168 kgP_2O_5 and 140 $kgK_2O \cdot ha^{-1}$ were introduced to the soil of fertilized treatments (except the control). To the soil fertilized with manure and organic materials, the whole nitrogen dose was introduced in the mentioned fertilizer and materials. Mineral fertilizers (ammonium nitrate 34 % N, enriched superphosphate 40 % P_2O_5 and potassium chloride 60 % K_2O) were used in order to introduce nutrients to the soil fertilized with mineral fertilizers as well as to even up the doses of phosphorus and potassium in the soil of the remaining fertilized treatments. These fertilizers were also used to conduct fertilization in the second and third years of the experiment, introducing 100 kgN, 30 kgP_2O_5 and 110 $kgK_2O \cdot ha^{-1}$ to the soil each year. Detailed data regarding conditions of conducting the experiment are included in the papers of Tabak and Filipek-Mazur [8, 9].

The content of trace elements in the organic materials used for fertilization did not exceed the limit values established for agricultural use of sewage sludge [5–7]. Table 1 shows nickel content in the manure and in the organic materials used for fertilization as well as doses of nickel introduced to the soil with manure and these materials.

Table 1

Nickel content in manure and in organic materials as well as doses of nickel introduced to soil with manure and materials

Material	Content [mgNi $\cdot$ kg^{-1} d.m.]	Dose [gNi $\cdot$ ha^{-1}]
Manure	4.49	25
Green waste compost	8.59	95
Sewage sludge	13.17	104
Compost from sewage sludge and straw	11.64	76
Mixture of sewage sludge and ash	15.43	170

The sewage sludge and the materials containing it had more of that element than the manure and the green waste compost. The highest nickel content was found in the mixture of sewage sludge and ash (15.43 mgNi $\cdot$ kg^{-1} d.m.), and with that mixture the biggest dose of the element (170 gNi $\cdot$ ha^{-1}) was introduced to the soil.

After harvest, the plant material was dried at a temperature of 70 $^{\circ}$C in a hot air dryer and milled. Then it was mineralized in a muffle furnace (8 h, 450 $^{\circ}$C), evaporated with hydrochloric acid solution, and the remains were diluted in nitric(V) acid solution [10]. The total nickel content in the air-dry soil sieved through a 1 mm mesh sieve was determined after incineration in a furnace (8 h, 450 $^{\circ}$C), evaporation with a mixture of concentrated nitric(V) and chloric(VII) acids, and dilution of the remains in hydrochloric acid [10]. The nickel content in the above-ground parts of maize and in the soil was determined with inductively coupled plasma atomic emission spectrometry (ICP-AES) on JY 238 Ultrace apparatus (Jobin Yvon).

Statistica software, version 10 (StatSoft, Inc.), was used for statistical elaboration of the results. A univariate analysis of variation was carried out, and the significance of differences between the mean values was estimated using the Duncan test ($\alpha \leq 0.05$).

Results and discussion

During the research, no nickel pollution of the above-ground parts of maize was found. Between 0.47 and 1.15 mgNi $\cdot$ kg^{-1} d.m. was determined in the plant material (Table 2), whereas the permissible content for plants intended for feed was established by Kabata-Pendias et al [11] to be 50 mgNi $\cdot$ kg^{-1} d.m.

The danger of considerable accumulation of nickel in the above-ground parts of maize is low as this plant stores collected trace element mainly in roots [12, 13].

A significant increase in the nickel content in maize as a result of fertilization was found only in the 2nd year of the research – maize fertilized with mineral fertilizers

Table 2

Nickel content in above-ground parts of maize [mgNi · kg^{-1} d.m. ± SD]

Treatment	1st year	2nd year	3rd year	Weighted mean content
No fertilization	$0.80^{bc*} \pm 0.12$	$1.02^{a} \pm 0.06$	$0.69^{d} \pm 0.03$	0.83
Mineral fertilizers	$0.74^{b} \pm 0.12$	$1.15^{b} \pm 0.04$	$0.51^{ab} \pm 0.03$	0.82
Manure	$0.72^{ab} \pm 0.06$	$1.11^{ab} \pm 0.08$	$0.54^{abc} \pm 0.03$	0.81
Green waste compost	$0.71^{ab} \pm 0.09$	$1.10^{ab} \pm 0.13$	$0.55^{bc} \pm 0.06$	0.80
Sewage sludge	$0.70^{ab} \pm 0.08$	$1.05^{ab} \pm 0.08$	$0.47^{a} \pm 0.06$	0.77
Compost from sewage sludge and straw	$0.58^{a} \pm 0.06$	$1.05^{ab} \pm 0.09$	$0.48^{ab} \pm 0.07$	0.71
Mixture of sewage sludge and ash	$0.93^{c} \pm 0.09$	$1.12^{ab} \pm \leq 0.00$	$0.59^{c} \pm 0.04$	0.90

* Mean values in columns marked with the same letters do not differ statistically significantly at $\alpha \leq 0.05$, according to the Duncan test; SD – standard deviation.

contained 13 % more nickel than the non-fertilized plants. In the 1st year, the plants fertilized with the compost from sludge and straw, and in the 3rd year all the fertilized plants contained significantly less nickel than the plants gathered from the control. It should be explain by accumulation of the element in the low yield of maize harvested from the control (a negative effect of the lack of fertilization on the amount of maize yield was found particularly in the second and third years of the research [9]). Maize fertilized with the mixture of sludge and ash was characterized by the highest mean weighted nickel content (by 8 % higher than the one found in maize gathered from the control treatment), whereas only plants fertilized with that mixture had a higher mean nickel content than the content determined in the non-fertilized plants.

Bibliographic data indicate a possibility to increase nickel content in plants fertilized with organic materials derived from waste. Such a relation was shown by, among others, Bhattacharyya et al [14] who grew rice on soil treated with municipal solid waste compost. Differently than in own research, Akdeniz et al [15] found an increase in nickel content in sorghum leaves as a result of fertilization with sewage sludge (however, content of the element in grains did not change after fertilization).

The amount of an element taken up with plant yield is a product of the content of that element in the yield and the size of that yield. In own research, dry matter yield from the above-ground parts of the fertilized plants was always higher than the yield harvested from the control treatment – depending on year and object of the research, the increase in yield as a result of fertilization reached between 9 and 88 % [9]. In consequence, despite a relatively high content of the component in the control plants, nickel uptake from the fertilized soil was generally higher than from the soil of the control treatment (particularly in the 1st and 2nd years of the research) (Fig. 1).

During three years of the research, the non-fertilized plants took up 38.0 g Ni · ha^{-1}. Total nickel uptake from the fertilized soil was higher by 13–47 % than the uptake from the control soil (the highest from the soil fertilized with mineral fertilizers, manure, green waste compost, and the mixture of sludge and ash).

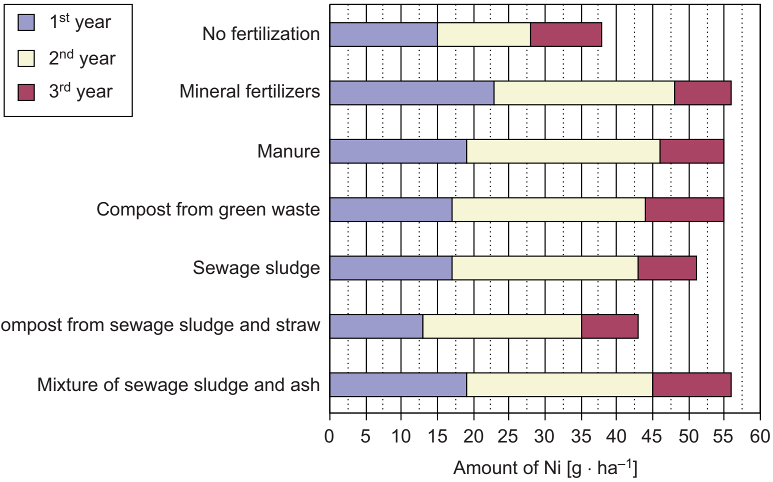

Fig. 1. Amount of nickel taken up by maize

Soil from the experimental field contained between 4.0 and 5.71 mg Ni · kg^{-1} d.m. (Table 3).

Table 3

Content of total forms of nickel in soil [mg Ni · kg^{-1} d.m. ± SD]

Treatment	1st year	2nd year	3rd year
No fertilization	4.36^{a}* ± 0.48	4.15^{ab} ± 0.06	4.26^{ab} ± 0.36
Mineral fertilizers	4.04^{ab} ± 0.74	4.03^{a} ± 0.52	4.10^{a} ± 0.58
Manure	5.08^{abc} ± 0.87	5.16^{d}± 0.24	5.04^{bc} ± 0.22
Green waste compost	5.36^{bc} ± 0.76	5.33^{d} ± 0.46	5.21^{c} ± 0.59
Sewage sludge	5.00^{abc} ± 0.65	5.00^{cd} ± 0.29	4.84^{abc} ± 0.66
Compost from sewage sludge and straw	4.68^{abc} ± 0.53	4.53^{bc} ± 0.68	4.66^{abc} ± 0.68
Mixture of sewage sludge and ash	5.71^{c} ± 0.05	5.41^{d}± 0.05	5.37^{c} ± 0.22

* See Table 2; SD – standard deviation.

No soil pollution with nickel was detected in any year of the research, because, as specified by Kabata-Pendias et al [16], natural nickel content in medium soil (which was examined in the own experiment) is up to 25–50 mg · kg^{-1} d.m., depending on soil pH values. Neither did the nickel content in the soil from the experimental field exceed the permissible level for soils of agricultural lands, established in the regulation on soil and earth quality standards [17] and amounting to 100 mgNi · kg^{-1} d.m. In addition, the nickel content was several times lower than the permissible content in soil, established for fertilization use of sewage sludge and amounting to 35 mgNi · kg^{-1} d.m. [7].

In all years of the research, the soil fertilized with the green waste compost as well as with the mixture of sludge and ash contained significantly more nickel than the non-fertilized soil. Depending on treatment and year of the research, that content was higher by 22–31 %.

When studying the effect of fertilization with composts from municipal sewage on nickel content in soil, Weber et al [18] generally did not show a statistically significant effect of the applied fertilization on the content of the element. Only application of a large dose of compost from municipal sewage from a strongly industrialized area led to an increase in nickel content in soil, although this effect occurred only in the year when the compost was used. Different results were obtained in own research where the green waste compost was used for fertilization. Wolejko et al [19], who used sewage sludge on city soils, found an increase in nickel content in the humus level (when comparing with the geochemical background value), although not to a content that would indicate soil pollution, according to Polish law. Antonkiewicz et al [20], who used a mixture of sewage sludge and fly ash for fertilization, did not find any changes in nickel content in soil. Own observations do not confirm these results.

When summarizing the presented results of own research, it should be emphasized that only soil fertilization with the mixture of sewage sludge and hard coal ash led to an increase in the nickel content in maize and soil. However, this effect was noticeable only in some years of the research, and fertilization with the mixture never led to pollution of plants and soil. From the materials used for fertilization, the mixture of sludge and ash had the highest nickel content. It resulted from a high nickel content in ash that was used for preparing the mixture; ash used in own research contained 24.9 $\mathrm{mgNi \cdot kg^{-1}}$ d.m.

As highlighted above, fertilization use of materials derived from waste with high content of trace elements results in an increase in the content of these elements in soil, and sometimes also in plants. Content of elements in a plant is, however, a derivative not only of their total content in soil, but also of the form of their occurrence (availability). In own research, a tendency for a higher nickel content in the plants fertilized with mineral fertilizers was observed. The content of the element taken up from soil of this treatment was also high (Table 2, Fig. 1). It was probably a result of higher acidification of the soil fertilized with mineral fertilizers and of lower organic matter content in that soil in comparison to the soil of the other treatments. This is because, along with a decrease in soil pH value and a decrease in organic matter content in soil, the availability of trace elements for plants increases [21, 22].

Conclusions

1. During the research no nickel pollution of the plants and soil was found.
2. A significant increase in the element content in maize as a result of fertilization was found only in the 2nd year of the research (maize fertilized with mineral fertilizers contained more nickel than the non-fertilized plants). In the 1st year, the plants fertilized with the compost from sludge and straw, and in the 3rd year all the fertilized plants contained significantly less nickel than the non-fertilized plants.
3. Only plants fertilized with the mixture of sewage sludge and ash had a higher mean nickel content than the content determined in the non-fertilized plants.

4. Total nickel uptake from the fertilized soil was higher than the uptake from the control soil (the highest from the soil fertilized with mineral fertilizers, manure, green waste compost, and the mixture of sludge and ash).

5. Fertilization with the green waste compost as well as with the mixture of sewage sludge and ash resulted in a statistically significant increase in the nickel content in the soil.

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ZAWARTOŚĆ NIKLU W KUKURYDZY I GLEBIE NAWOŻONEJ MATERIAŁAMI ORGANICZNYMI POCHODZENIA ODPADOWEGO

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Abstrakt: Badania przeprowadzono w celu określenia wpływu nawożenia odpadowymi materiałami organicznymi na zawartość i pobranie niklu przez kukurydzę oraz na ogólną zawartość niklu w glebie. Trzyletnie doświadczenie polowe obejmowało 7 obiektów: glebę nienawożoną (kontrola) oraz glebę nawożoną nawozami mineralnymi, obornikiem bydlęcym, kompostem z odpadów zielonych, osadem ściekowym, kompostem z osadu ściekowego i słomy oraz mieszaniną osadu ściekowego i popiołu z węgla kamiennego. Zawartość niklu w częściach nadziemnych roślin i glebie oznaczono metodą ICP-AES.

W trakcie prowadzenia badań nie stwierdzono zanieczyszczenia roślin i gleby niklem. Istotne zwiększenie zawartości pierwiastka w kukurydzy w wyniku nawożenia stwierdzono tylko w II roku badań, po nawożeniu nawozami mineralnymi. W I roku rośliny nawożone kompostem z osadu i słomy, a w III roku wszystkie nawożone rośliny zawierały istotnie mniej niklu od roślin zebranych z obiektu kontrolnego. Największą średnią ważoną zawartością pierwiastka cechowała się kukurydza nawożona mieszaniną osadu i popiołu. Sumaryczne pobranie niklu z gleby nawożonej było większe od pobrania z gleby kontrolnej. Gleba nawożona kompostem z odpadów zielonych oraz mieszaniną osadu i popiołu zawierała istotnie więcej niklu od gleby nienawożonej.

Słowa kluczowe: odpadowe materiały organiczne, osad ściekowy, kompost, nikiel, pierwiastki śladowe

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EXAMINATION OF THERMAL STABILITY OF WASTE ROCKWOOL AND AMMONIUM NITRATE MIXTURES

BADANIE STABILNOŚCI TERMICZNEJ MIESZANIN ODPADOWEJ WEŁNY MINERALNEJ I AZOTANU AMONU

Abstract: Results of research carried out on a waste rockwool and ammonium nitrate mixtures to examine the possibility of using them in fertilization of plants were presented. Reactions occurring between compounds were analyzed to determine the possibility of an uncontrolled exothermic decomposition of nitrogen fertilizer additive. Results obtained from the analysis of prepared mixtures in various proportions and separate samples of individual compounds were compared. Ammonium nitrate used in the research was supplied by one of the domestic fertilizers producer and waste rockwool was collected after a completed crop cycle of a tomato plant. Each sample was dried and ground before examination. Analysis was carried out using differential thermal analysis coupled with thermogravimetry and mass spectrometry (DTA-TG-MS). Obtained results indicate a possibility of use of rockwool mixed with ammonium nitrate in agriculture. However, it is important to choose optimal proportions of compounds to ensure the thermal stability of the mixture.

Keywords: ammonium nitrate, rockwool, thermal analysis, fertilizers, agriculture, decomposition

Introduction

Rockwool is obtained by melting basalts and dolomites. Rocks are being melted, stretched and rolled. A rockwool consists of amorphous fibers of thin diameter coated with binders and additives [1, 2]. Binders, such as phenol-formaldehyde resin, allow convenient shaping of the product. Impregnating oils and coating agents can be distinguished among other additives. The total organic content in the rockwool is about 2–4 wt %. This material is mainly used as an insulation or a hydroponic base for cultivation in gardening. It has a lot of advantages like a good stabilization of pH, temperature and moisture. In comparison to an organic base, rockwool shows lesser

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vulnerability to expansion of pathogens, which makes spreading of plant diseases less likely to happen [3]. Inert soil substitutes are usually replaced after each cultivation cycle due to deterioration of their physical properties after this time [4, 5]. However, it is sometimes being reused two or three times before wasting, which can influence quality of growing plants [6]. Rockwool is not an easy substance to dispose of. There are many ongoing researches aimed at viable recycling methods, because after a completed crop cycle, waste rockwool contains some amounts of residual nutrients [7]. Possibility of using a mixture of waste rockwool with a suitable amount of fertilizer is considered.

Ammonium nitrate is a chemical of a great practical importance. Among all nitrogen fertilizers, it is produced in the largest amounts [8]. Nitrogen contained in fertilizers is present in two forms – nitrate, which is assimilated immediately, and ammonium, that is retained in the ground and made available to plants after a prolonged period of time. The use of ammonium nitrate improves the quantity and quality of the crop and increases the weight of the above ground plant parts [9]. In order to ensure the optimal efficiency of fertilization, ammonium nitrate should be mixed with the soil. One of its drawbacks is the tendency to explosive decomposition, which is a real threat that must be strictly controlled [10]. Due to its properties, it is commonly used as an explosive material for miners in form of porous granules soaked in fuel oil. Before using any mixtures of ammonium nitrate with other components, for safety reasons, the influence of these additives on the thermal stability of the fertilizer must be examined [11, 12].

Thermal analysis allows to determine the temperature range of physical or chemical changes, which are associated with thermal effects in tested materials. This allows to assess in which temperatures it is safe to store such materials without any risk of occurrence of unwanted processes [13]. Additionally, thermal analysis demonstrates how examined materials change their thermal properties, depending on the mass ratio of the individual components in the test samples [14].

Materials and methods

The present study uses ammonium nitrate of fertilizer grade, supplied by one of the domestic producers of nitrogen fertilizers. The rockwool was collected after a completed one-year crop cycle of tomatoes, air-dried and ground on a sieve of 0.4 mm diameter. An analysis of 100 mg (± 0.5 mg) samples was performed. Samples consisted of 20 mg of ammonium nitrate and 80 mg of rockwool (sample WM80AN20) and in reverse ratios (sample WM20AN80). Prior to measurement, the mixtures were thoroughly triturated in a mortar in order to homogenize their composition.

The measurements were performed using differential thermal analysis and thermogravimetry coupled with mass spectrometry (DTA-TG-MS). Thermal analyzer STA 449 F3 with thermobalance and a mass spectrometer QMS 403 C, Netzsch were used. The samples were tested in crucibles of 0.3 cm^3 capacity made of alumina.

The measurements consisted of several consecutive steps. The first one was heating the empty crucible in order to remove any possible impurities, then a correction conducted to compensate for thermal effects associated with the characteristics of the crucible. Afterwards, the crucible with the sample was heated to selected temperature at a rate of 5 °C/min in the atmosphere of synthetic air with a total flow of 60 cm^3/min. Before each correction and measurement, a proper evacuation of gas from the furnace chamber was performed and followed by filling it with a synthetic air. This sequence was repeated three times before each measurement.

For comparison purposes, samples of 100 mg (± 0.5 mg) ammonium nitrate and 100 mg (± 0.5 mg) waste rockwool were examined according to the same methodology. Results were analyzed using software supplied by the manufacturer of the measuring equipment.

Results and discussion

The aim of this study was to investigate the possibility of reusing in a fertilization the waste rockwool derived from tomatoes cultivation. Thermal properties of mixtures of ammonium nitrate with waste rockwool were examined. Ammonium nitrate, the compound used in fertilizing to provide plants with necessary nitrogen, may undergo a rapid decomposition in contact with various organic compounds [15]. In order to avoid undesired exothermic reactions, it was necessary to investigate the influence of binders contained in a rockwool on the decomposition of ammonium nitrate.

Fig. 1 shows the result of thermal analysis of waste rockwool sample, while Fig. 2 shows the result of measurement carried out for ammonium nitrate. Both analyzes were

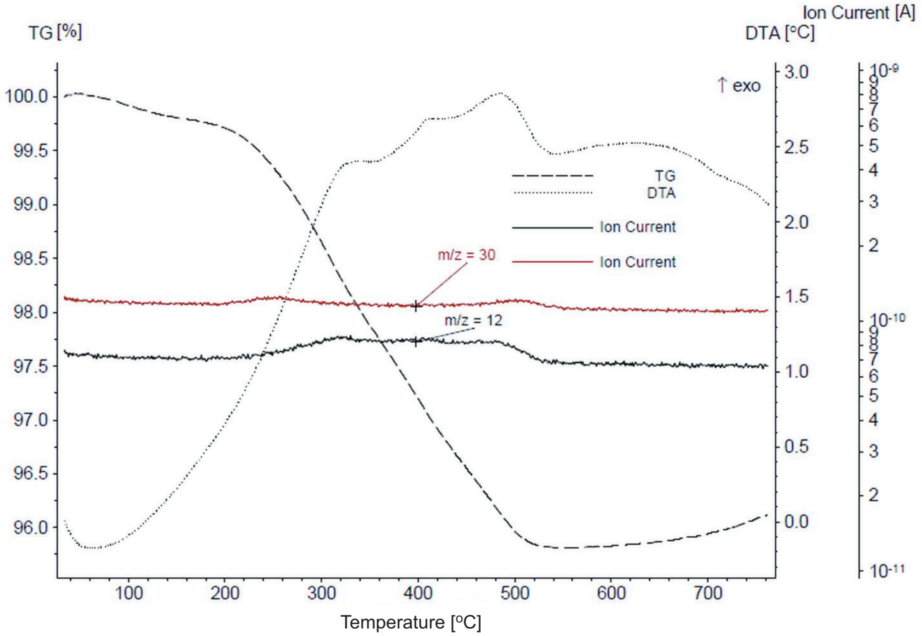

Fig. 1. DTA-TG-MS results for a 100 mg sample of a waste rockwool

performed in order to determine the optimal temperature range for the examination of selected mixtures (WM80AN20 and WM20AN80).

The first step of weight loss of a rockwool sample observed in the range of 50–200 °C is associated with vaporization of water and did not exceed 0.2 % of the total mass. Another weight loss was observed over 230 °C and was accompanied with an exothermic effect caused by an oxidation of organic binder. The observed weight loss due to burnout of the binder is typical for organic compounds content in rockwool which is ca. 4 % of the total mass. MS signal for carbon dioxide (*m/z* = 12) and the DTA signal clearly indicate the combustion of the binder with heat generation, while no changes in signal for nitrogen oxides (*m/z* = 30) show that there are no significant amounts of nitrogen compounds present in examined sample. The decomposition ends at a temperature slightly above 500 °C. The mass gain over 650 °C is related to the oxidation of the silicate groups in the rockwool [16]. Above this temperature there are no relevant reactions occurring [17].

Examined sample of ammonium nitrate showed no significant deviations from thermal properties of this compound reported in the literature [9]. Endothermic phase transitions typical for ammonium nitrate can be observed on the DTA curve shown in Fig. 2. Afterwards, the exothermic decomposition of the test sample occurs in the temperature range from 230 °C to 300 °C. MS signal for carbon dioxide shows that there were no organic impurities in ammonium nitrate, while signal *m/z* = 30 confirms the evolution of significant amounts of nitrogen oxides due to the decomposition of fertilizer.

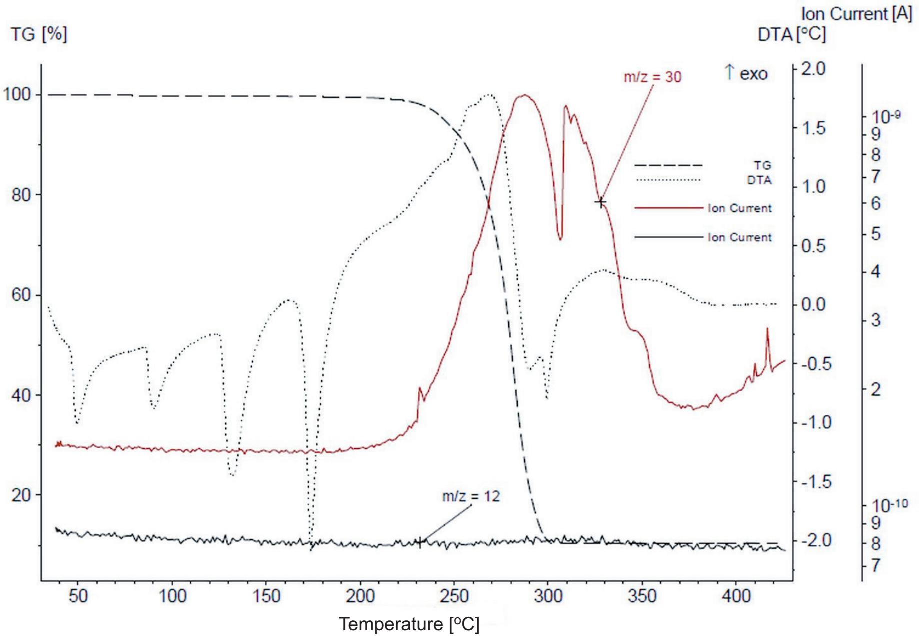

Fig. 2. DTA-TG-MS results for a 100 mg sample of a fertilizer grade ammonium nitrate

Results of thermal analysis of tested mixtures of ammonium nitrate and rockwool in two different proportions are presented in Fig. 3 and Fig. 4. The range of temperature in those measurements was chosen based on previous analyzes. Thermal analysis of tested samples revealed that their exothermic decomposition occurs more rapidly and in lower temperature than decomposition of pure components. Exothermic decomposition began in 205.7 °C and lasted until around 500 °C for the WM80AN20 sample. It is possible to distinguish two stages of exothermic decomposition of the studied mixtures. The decomposition of ammonium nitrate with a part of organic binder, that lasted up to about 270 °C, was the first stage. The second one, occurring over 400 °C, was accompanied with burning of the residual organic binder contained in a rockwool. Compared to pure components, the examined sample showed reduced thermal stability. It proves that ammonium nitrate interacts with organic compounds from rockwool, which is also evidenced by simultaneous evolution of carbon dioxide and nitrogen oxides.

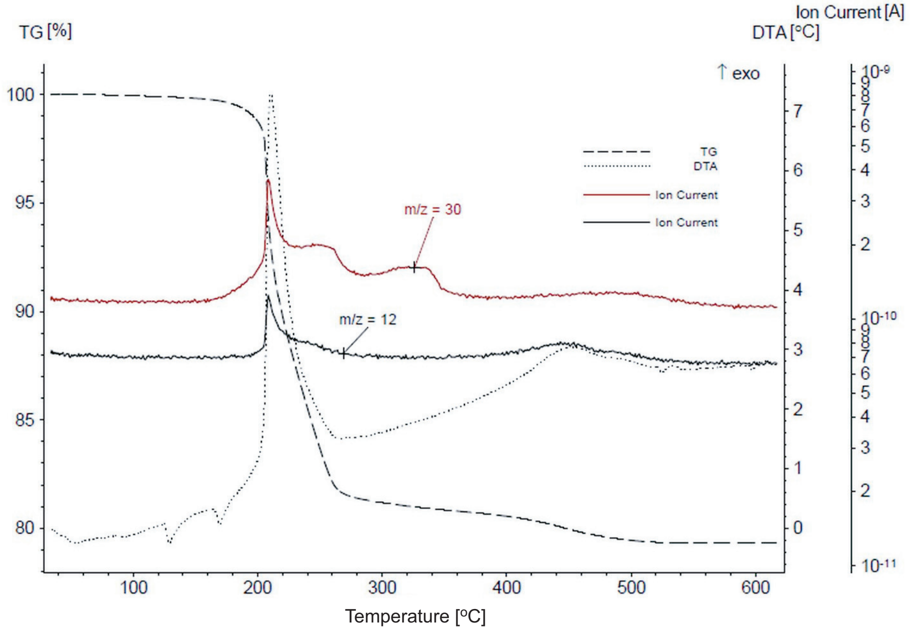

Fig. 3. DTA-TG-MS results for a 100 mg WM80AN20 sample

In sample WM20AN80, the decomposition began in 204.3 °C and observed reactions occurred in temperature ranges similar to WM80AN20 sample. However, it was possible to notice a dominance of decomposition of ammonium nitrate over processes related to organic binder. The rate of the heat generation in that sample was also lower. This effect may be associated with a smaller amount of an organic binder in the sample, not high enough to cause as strong exothermic reaction with ammonium nitrate as in the case of WM80AN20.

MS signal for carbon (*m/z* = 12), originating from carbon dioxide generated from the decomposition of an organic binder, and signal for nitrogen oxides (*m/z* = 30), from the decomposition of ammonium nitrate, were qualitatively similar and occurred at approximately the same temperature range for both tested mixtures. It can be noted that above 200 °C there are present both nitrogen oxides and carbon dioxide in exothermic reaction products. This is a confirmation of the simultaneous decomposition of ammonium nitrate and an organic binder contained in the rockwool. It may have an adverse influence on thermal stability of mixtures. Intensity of an exothermic reaction depends on proportions of components in examined samples.

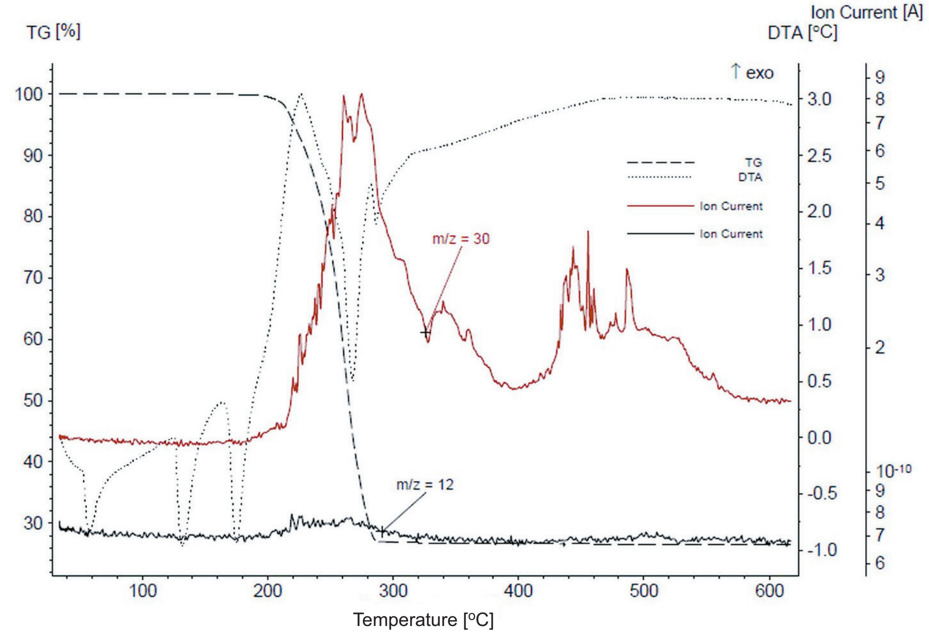

Fig. 4. DTA-TG-MS results for a 100 mg WM20AN80 sample

Table 1 presents temperatures of phase transitions and exotherm maximum in examined samples. Mixtures of ammonium nitrate and rockwool were melting in a slightly lower temperature than pure ammonium nitrate. The maximum rate of their exothermic decomposition was also reached earlier. Exotherm maximum for WM80AN20 sample was at 210.6 °C, which is the lowest temperature among all examined samples.

Table 1

Results of thermal analysis of samples containing ammonium nitrate

Sample	Temperature of phase transitions [°C]				Exotherm maximum [°C]
	IV → III	III → II	II → I	Melting	
Ammonium nitrate	46.8	86.5	126.0	169.8	268.2
WM80AN20	—	—	125.9	166.4	210.6
WM20AN80	53.2	—	126.3	168.3	226.4

Conclusions

Based on performed research, it can be concluded that the interactions between ammonium nitrate and organic binder contained in an inert rockwool result in a higher intensity and lower temperature of the beginning of thermal decomposition of ammonium nitrate. The observed exothermic reactions in studied mixtures occur at a lower temperature than decompositions of individual components, which shows a clear synergetic effect. It is possible that ammonium nitrate, as a strong oxidant, causes burning of an organic binder at temperature above 200 ^{o}C. This fact may reduce the safety during improper usage and storage of this type of mixtures. However, the possibility of safe usage of mixtures with different mass proportions cannot be excluded, which is a basis for a further research. This means that the selection of appropriate proportions of such mixtures cannot be based solely on the needs of plants for nutrients contained in fertilizers. Safety issues associated with destabilizing effects of rockwool's binder on ammonium nitrate should also be taken under consideration.

Acknowledgements

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BADANIE STABILNOŚCI TERMICZNEJ MIESZANIN ODPADOWEJ WEŁNY MINERALNEJ I AZOTANU AMONU

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Abstrakt: Przedstawiono wyniki badań przeprowadzonych dla mieszanin odpadowej wełny mineralnej z azotanem(V) amonu w celu przeanalizowania możliwości zastosowania ich w nawożeniu. Zbadano zachodzące w mieszaninach przemiany fizykochemiczne, co umożliwiło określenie ryzyka zajścia gwałtownego egzotermicznego rozkładu azotowego komponentu mieszanki. Porównane zostały wyniki uzyskane z analiz mieszanin azotanu(V) amonu z odpadową wełną mineralną w różnych proporcjach masowych oraz oddzielnych próbek poszczególnych składników. Stosowany azotan(V) amonu pochodził od krajowego producenta nawozów, natomiast wełna mineralna została uzyskana po jednorocznym cyklu uprawy pomidora. Do przeprowadzenia analizy zachodzących w badanym układzie przemian zastosowano różnicową analizę termiczną sprzężoną z termograwimetrią i spektrometrią mas (DTA-TG-MS). Uzyskane wyniki wskazują na możliwość wykorzystania odpadowej wełny mineralnej w mieszance z azotanem(V) amonu w rolnictwie. Należy jednak odpowiednio dobrać skład mieszaniny, biorąc pod uwagę jej stabilność termiczną.

Słowa kluczowe: azotan amonu, wełna mineralna, analiza termiczna, nawozy, rolnictwo, rozkład

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ASSESSMENT OF THE EFFECT OF ENVIRONMENTAL VARIABLES ON HEALTH STATUS OF *Tilia cordata* Mill. IN PARKS

OCENA WPŁYWU ZMIENNYCH ŚRODOWISKOWYCH NA STAN ZDROWOTNY LIPY DROBNOLISTNEJ W PARKACH

Abstract: Analyses concerned the effect of different environmental variables on the health status of little-leaf linden (*Tilia cordata* Mill.). The study comprised analyses and statistical models based on discriminatory analysis. These analyses indicated which variables may influence the health status of tress of the investigated species in the parks of Poznan. The model was based on the canonical variate analysis (CVA), *ie* Fisher's canonical variant of linear discriminatory analysis (LDA). The greatest negative effect on the health status of trees of *Tilia cordata* Mill. in Poznan parks was found for the small distance of the parks from the city centre and the immediate vicinity of two arterial roads. It was also found that the vicinity of buildings heated with fossil fuels, primarily coal, may have had a negative effect on the health status of *Tilia cordata* Mill. trees in the Poznan parks. Moreover, it was shown that specimens of the investigated species aged 81–120 years were characterised by the worst health status, while the best health condition was found in trees of *Tilia cordata* Mill. in the Millennium Park.

Keywords: urbanized areas, environmental changes, Poznan, statistical models

Introduction

The air quality in cities is a problem in view of the expansion of urbanised zones [1], [2]. Soil moisture, the content of nutrients as well as pathogens and pests have been found to influence the processes related with defoliation of tree crowns [2]. The trees in public open spaces have been proved to have influence on accumulation and retention of water and groundwater [3–8]. Studies have proved that trees growing in cities may reduce the pollution with O_3, SO_2, CO, NO_x and suspended particulate matter [9–14].

Under natural conditions of Poland *Tilia cordata* Mill. is a component of fertile, multi-species deciduous forests shedding leaves for winter. Under optimal conditions and

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in a compact stand it may reach a height of 38–42 m at stem diameter exceeding 200 cm. It is also of importance that trees from the genus *Tilia* do not form permanent, pure stands, although they may dominate in a multi-species stand. Trees of *Tilia cordata* Mill. prefer moist, permeable and fertile soils and tolerate the presence of calcium in soil. It was stated experimentally that the length of vegetation phases in the described species is influenced, among other things, by precipitation, insolation and winds. It was also found that the length of vegetation phases of *Tilia cordata* Mill. is more strongly affected by the number of cloudless days and the number of days with rainfall than annual precipitation total. It was also confirmed that weather with heavy rains and rapidly passing cloud cover is more advantageous for growth of this tree species that the weather with a lasting cloud cover and an extensive period of rainy weather [15]. It was also observed that the most advantageous living conditions for *Tilia cordata* Mill. are found in localities with predominant south-western and western winds. Trees from the genus *Tilia* are also relatively drought-resistant, being more resistant than trees from genera *Betula*, *Alnus* or *Carpinus*, but less resistant than trees from the genera *Fraxinus*, *Quercus* or *Sorbus* [16, 17].

Trees from the genus *Tilia* should be used in high greenery in residential districts and parks, while these trees were not recommended in planting of streets and squares due to the difficult environmental conditions. A more extensive application could be found for trees from the genus *Tilia* in countryside plantings, particularly as roadside trees [18, 19].

Threats to *Tilia cordata* Mill. trees in urbanised areas

Air pollution under urban conditions has an adverse effect on the activity of the shoot apex, which leads to a reduced leaf area or the appearance of double buds. In the experiments performed on trees of the investigated species it was found that trees of *Tilia cordata* Mill. are sensitive to the action of SO_2 and acid rain. The considerable reduction of photosynthetic activity was also observed in the environment polluted with fluorine. Elevated Na, Cl, Ca, Mg, Zn and Cu rates as well as elevated soil pH have a negative effect on the health status of trees of that species growing in the vicinity of traffic routes. Increased salinity or EC, caused by the elevated Na and Cl levels, also have a detrimental effect on trees of *Tilia cordata* Mill. and other species, resulting – particularly in spring – in the so-called physiological drought [20–22]. Trees of this species are also relatively resistant to air pollution in urbanised areas, as a greater seasonal accumulation of Cr, Fe, Ni and Pb ions in leaves than that in *Tilia cordata* Mill. is observed in trees of *Aesculus hippocastanum* L. *Tilia cordata* Mill. was not observed to accumulate Cu ions in its leaves. In contrast, trees of *Tilia cordata* Mill. are less resistant to air pollution in urbanised areas than trees from the genera *Carpinus* and *Robinia* [23]. It was also found that trees of *Tilia cordata* Mill. are markedly less sensitive to ozone air pollution than trees of *Salix alba* L., *Tilia platyphyllos* Scop. or *Fraxinus excelsior* L. [24].

Methods

Analyses covered public parks of historic value in the city of Poznan, in which the share of *Tilia cordata* Mill. trees was considerable. These parks include (the numbers follow those in Fig. 1):

1. The Polish State Millennium Park – the share of *Tilia cordata* Mill. trees in the park stand is 0.7 %,
2. The Park between Czecha and Rusa Housing Estates – the share of trees of the analysed species in the park stand is 1.3 %,
3. The John Paul II Park – the share of trees of the described species in the park stand is 5.1 %,
4. The Gorczynski Park – the share of *Tilia cordata* Mill. trees in the park stand is 38.8 %,
5. The Rev. Joseph Jasinski Park – the share of trees of the analysed species in the park stand is 2.4 %,
6. The Gustaw Manitius Park – the share of trees of the described species in the park stand is 12.9 %.

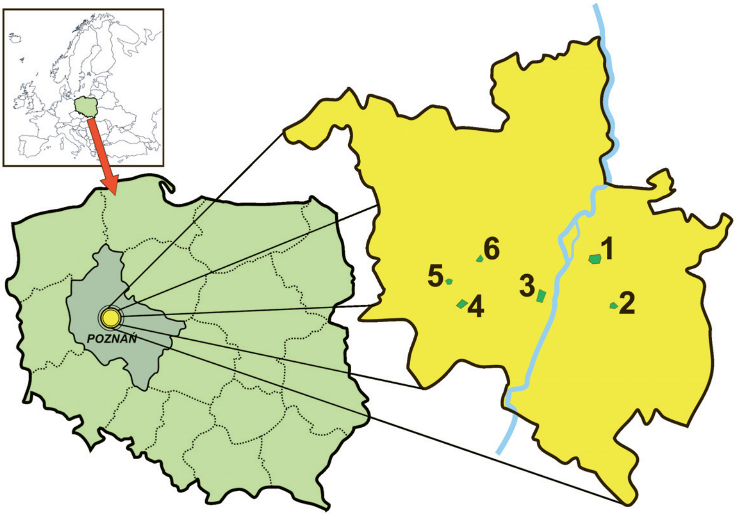

Fig. 1. Maps indicating the location of Poland in Europe, location of Poznan in Poland and a map of the city of Poznan with marked locations of parks analysed in this study (author of the maps: M. T. Walerzak)

Two of the above mentioned objects are parks established in the area of former forts of the outer ring of Prussian fortifications from the second half of the 19th century (the parks between the Czecha and Rusa Housing Estates, and the Rev. Joseph Jasinski Park), while two other parks were formed from the transformation of former Evangelical cemeteries (the Gorczynski Park and the Gustaw Manitius Park).

Field studies connected with the survey of *Tilia cordata* Mill. trees growing in the selected parks were conducted in the years 2010–2012 in the summer period (June–August). In the course of survey studies the following characteristic elements were recorded:

1. stem circumference of each tree (measured at a height of 130 cm above ground), while in the case of multi-stem trees, forked below the height of 130 cm each stem was measured separately;

2. crown diameter of each tree (in the case of trees with irregular crowns two extreme diameters were measured and their mean was calculated);

3. height of each tree;

4. health status of examined trees – health status was evaluated based on criteria for tree condition evaluation [25], taking into consideration the condition of the crown, stem and roots of the tree.

Statistical analyses and models were developed based on discriminatory analysis. The conducted analyses verified which variables may influence the health status of *Tilia cordata* Mill. trees in the parks of Poznan. The model was constructed using canonical variate analysis (CVA), *ie* a canonical variant of Fisher's linear discriminatory analysis (LDA) [26].

The discriminatory analysis was used to compare the effect of different variables on the health status of specimens in the examined parks. Parameters included in the analyses comprised distance of the parks from the city centre, vicinity of industrial areas, traffic routes, watercourses and water bodies as well as incorporation of the parks into the municipal green system, emission of gases from combustion of fossil fuels by households neighbouring with the parks or original use of the areas in which the analysed parks were established.

In order to verify which variables to the greatest degree determine the health status of *Tilia cordata* Mill. trees in the Poznan parks the progressive step-wise analysis was applied. All variables were assessed and next these variables were included into the model, which contributed most to the discrimination of groups based on values of p and F for the analysed variable. This process is repeated to the moment when value p dropped below 0.05 for the examined variable.

In order to determine the boundary level of significance the Monte Carlo permutation test (separately for each variable and next for the entire model). All lists, calculations and graphic elements were performed in the Canoco for Windows programme and the Microsoft Excel spreadsheet. The following tools of the Canoco for Windows package were used: Canoco for Windows 4.5, CanoDraw for Windows and WCanoIMP.

Results

Analysis of recorded results made it possible to identify differences concerning morphometric parameters and health condition of trees of *Tilia cordata* Mill. living in selected parks of the city of Poznan (Fig. 2). The most impressive specimens in terms of height and crown width were reported in 3 parks (the Gorczynski, the Rev. Joseph Jasinski and the Gustaw Manitius parks), they were the oldest specimens among the examined trees. Some specimens exceeded 25 m in height, while their crown width was over 17 m (Table 1). In terms of health condition the best specimens were those found in the Polish State Millennium Park, with the averaged health condition score Q of 1.14 and it was close to health class I. Trees of this species in the Gustaw Manitius Park had the lowest health condition class, with classes III and II predominating. Circumferences of the examined trees were correlated with their age and ranged from 12 cm to 233 cm.

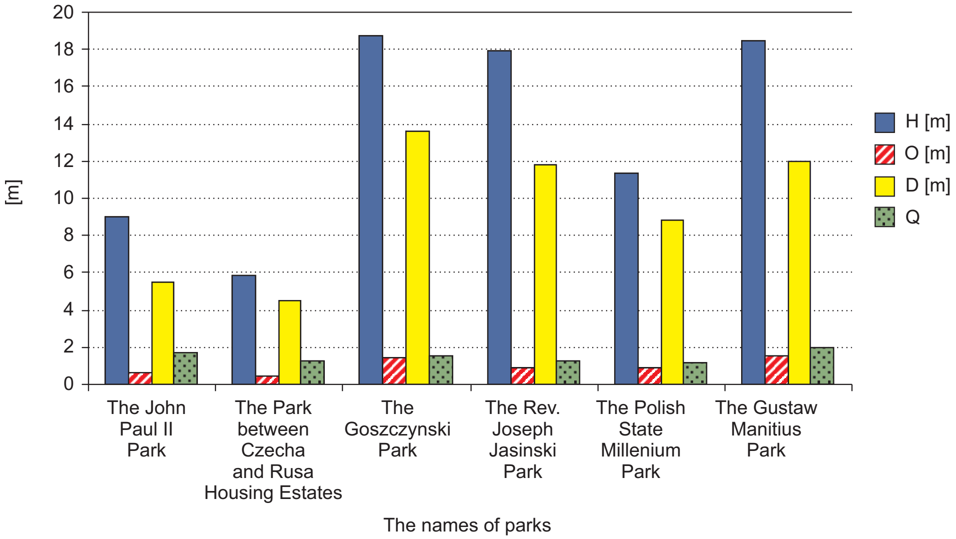

Fig. 2. Averaged values of analysed parameters for *Tilia cordata* Mill. in examined parks of the city of Poznan (H – tree height, O – stem circumference, D – crown diameter, Q – health condition)

Table 1

Minimum, maximum and mean values, and standard deviation for analysed parameters of *Tilia cordata* Mill. in Poznan parks

		H [m]	O [cm]	D [m]	Q			H [m]	O [cm]	D [m]	Q
The John Paul II Park	Min	3.5	23	2.5	1	The Rev. J. Jasinski Park	Min	7	35	4	1
	Max	16	159	10	5		Max	24	124	18	2
	$\bar{x}$	9.05	67.41	5.49	1.69		$\bar{x}$	17.90	92.80	11.80	1.30
	SD	2.90	25.99	1.53	0.81		SD	4.61	26.38	4.42	0.48
The Park between Czecha and Rusa Housing Estates	Min	2	13	1.8	1	The Polish State Millenium Park	Min	4	11.5	1.5	1
	Max	8	75	6.2	2		Max	20	168	13	2
	$\bar{x}$	5.83	45.90	4.47	1.25		$\bar{x}$	11.36	86.93	8.82	1.14
	SD	1.60	16.22	1.14	0.44		SD	3.80	30.24	2.28	0.35
The Gorczynski Park	Min	5	12	4	1	The Gustaw Manitius Park	Min	3.5	12	1.5	1
	Max	27	232	20	4		Max	22	233	17	3
	$\bar{x}$	18.78	142.69	13.63	1.57		$\bar{x}$	18.44	153.65	11.97	1.94
	SD	3.67	36.11	3.79	0.67		SD	3.35	40.92	3.25	0.77

H – tree height, O – stem circumference, D – crown diameter, Q – health condition.

The conducted statistical analysis showed a marked correlation (both positive and negative) for the distribution of environmental variables such as distance of the parks from the city centre, vicinity of traffic routes or industrial areas with the health status of the analysed species in the Poznan parks (Fig. 3). The greatest negative effect on the health condition of *Tilia cordata* Mill. trees in the Poznan parks was observed for such variables as distance of the parks from the city centre (with the worst health condition in specimens found in parks located within the radius of <2 km from the centre of Poznan). Moreover, a negative effect on the health condition for the examined species in the Poznan parks was recorded for the vicinity of traffic routes, running directly on both sides of the examined parks. The best health status was found for trees of *Tilia cordata* Mill. living in the parks, which were located farthest from the city centre (within the radius over 3 km), in the vicinity of which there were no industrial areas, while the parks were adjacent to one traffic route.

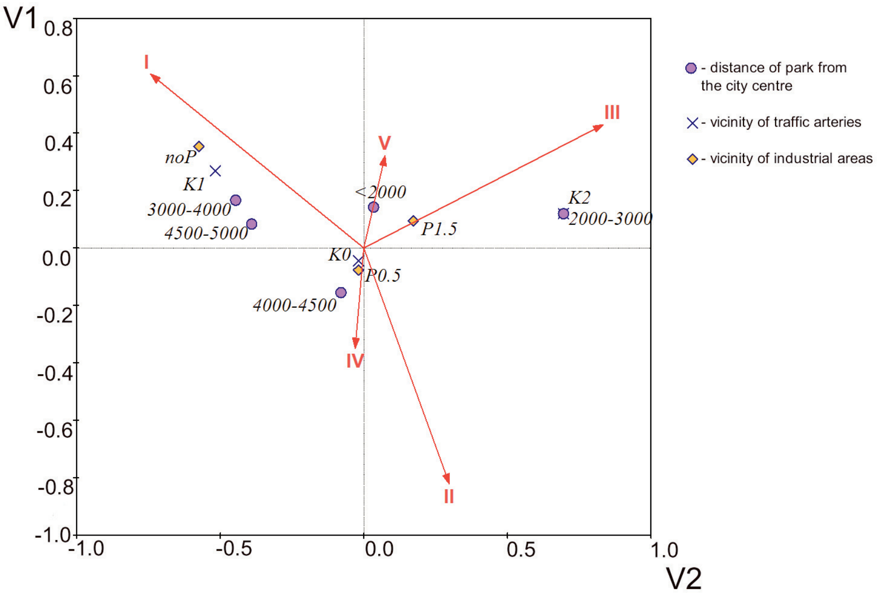

Fig. 3. The CVA model ($n = 340$) – dependencies between health condition of *Tilia cordata* Mill. in the Poznan parks and location of parks, vicinity of industrial areas, traffic arteries as well as watercourses and water reservoirs [2000–3000 – distance of park from the city centre; K0, K1, K2 – vicinity of one (two) traffic arteries; P0.5; P1.5 – vicinity of industrial areas at 0, <0.5 and <1.5 km; vicinity of watercourses and water reservoirs ($p < 0.05$)

The health condition of *Tilia cordata* Mill. trees living in the selected parks of Poznan was considerably affected by the heating method used in the residential buildings located in the adjacent areas. The vicinity of housing districts heated with fossil fuels, mainly carbon, could have had a negative effect on the health status of trees of the analysed species in the parks of Poznan. At the same time no potential negative effect was observed for the housing districts with the central heating system on the health status of the analysed species in the Poznan parks. In turn, no considerable correlation as a stimulant or destimulant was found between the health condition of *Tilia cordata* Mill. trees and the location in the wedge-ring system of the municipal green in Poznan. As it results from the above graph (Fig. 4), the health status of trees of the analysed species found in the area of former fortifications was class I, which could have been caused by the ring fortification system and the considerable distance from the city centre (no effect of urbanization factors).

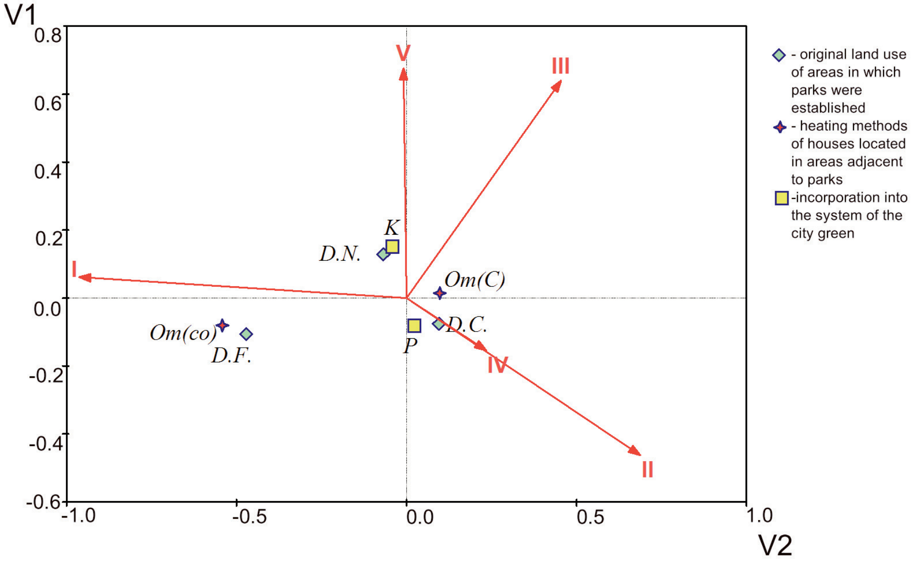

Fig. 4. The CVA model ($n = 340$) – dependencies between health condition of *Tilia cordata* Mill. in the Poznan parks and original land use of areas in which parks were established, heating methods of houses located in areas adjacent to parks and incorporation into the system of the city green [D.N. – former wasteland, D.C. – former cemeteries, D.F. – former forts; Om(co) – housing districts with central heating system, Om(C) – housing districts heated using fossil fuels; K – parks incorporated into green wedges, P – parks incorporated into green rings ($p < 0.05$)

The following model presents dependencies between the health status of *Tilia cordata* Mill. trees in the selected parks of the city of Poznan and the age ranges for individual specimens. As it results from the model given below (Fig. 5), the best health status was found for the youngest specimens belonging to the age ranges of 21–30 and 11–20 years. The worst health condition was found for lindens aged from 81 to 90 years. The greatest number of specimens belonging to health class IV was recorded for the age group from 111 to 120 years. Health class III was represented mainly by lindens aged from 91 to 100 years.

Health condition of *Tilia cordata* Mill. trees in the selected parks of the city of Poznan was influenced by many environmental conditions, as it was shown by the above models. Definitely the best health status was found for trees of the analysed species growing in The Polish State Millennium Park (Fig. 6). This park had optimal location

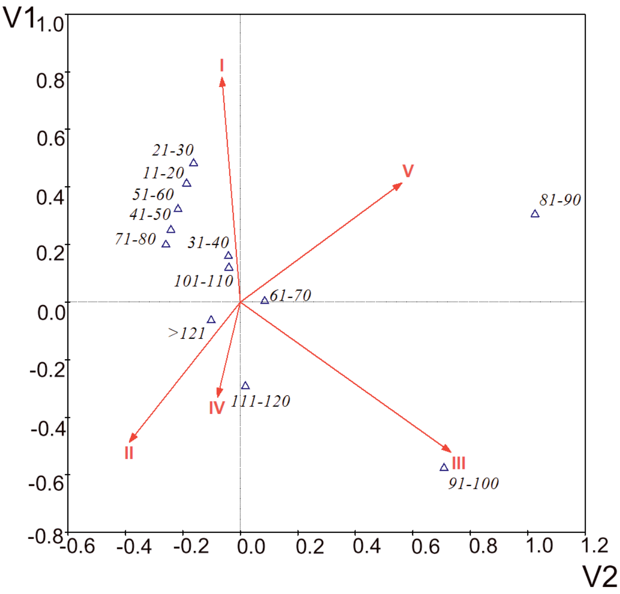

Fig. 5. The CVA model (n = 340) – dependencies between health condition of *Tilia cordata* Mill. in the Poznan parks and age of analysed trees ($p < 0.05$)

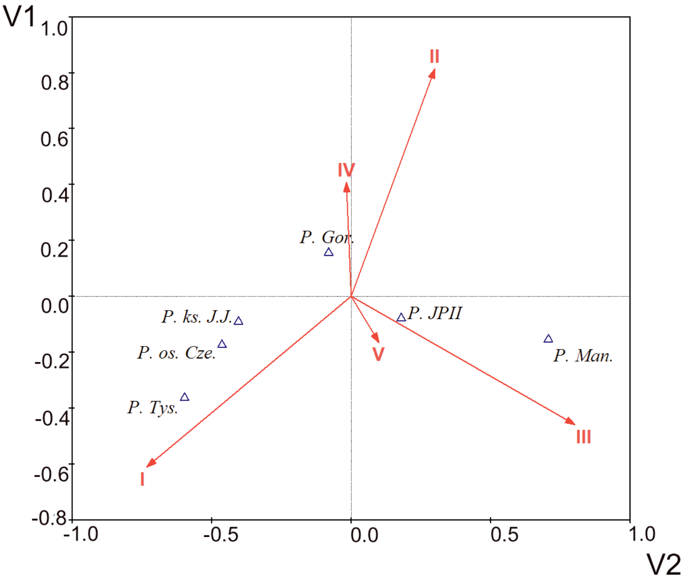

Fig. 6. The CVA model (n = 340) – dependencies between health condition of *Tilia cordata* Mill. in Poznan parks and analysed parks [P. Gor. – The Gorczynski Park, P. Tys. – The Polish State Millennium Park, P. Ks. J. J. – The Rev. J. Jasinski Park, P. Man. – The Gustaw Manitius Park, P. JPII – The John Paul II Park, P. os. Cze. – Park between Czecha and Rusa Housing Estate] ($p < 0.05$)

conditions, which resulted in a very good health status of the examined species. The Gustaw Manitius Park and the Jan Paweł II Park were those parks, in which *Tilia cordata* Mill. trees had the worst health status in comparison to the other analysed objects.

Conclusions

1. The greatest negative effect on the health condition of lindens in the parks of the city of Poznan was found for the distance of the parks from the city centre and the immediate vicinity of two traffic routes.
2. A statistically significant difference was found in the health status of lindens in relation to the heating method used in the housing buildings in the adjacent areas. Coal-heated housing districts could have had a negative effect on the health status of *Tilia cordata* Mill. trees in the Poznan parks.
3. Specimens aged 81–120 years old had the worst health status.
4. Trees of *Tilia cordata* Mill. found in The Polish State Millennium Park were characterised by the highest health status.
5. The most impressive specimens in terms of their height, stem circumference or crown width were reported in two parks: The Gorczynski Park and The Gustaw Manitius Park.

Acknowledgements

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OCENA WPŁYWU ZMIENNYCH ŚRODOWISKOWYCH NA STAN ZDROWOTNY LIPY DROBNOLISTNEJ W PARKACH

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Abstract: Badania dotyczyły wpływu różnych zmiennych środowiskowych na stan zdrowotny lipy drobnolistnej (*Tilia cordata* Mill.). W pracy wykorzystano analizy i modele statystyczne stworzone w oparciu o analizę dyskryminacyjną. Wynikiem przeprowadzonych analiz było wykazanie, które zmienne mogą wpływać na stan zdrowotny drzew badanego gatunku na terenie parków Poznania. Do skonstruowania modelu wykorzystano analizę CVA (canonical variate analysis) – kanoniczną odmianę liniowej analizy dyskryminacyjnej Fishera (LDA). Stwierdzono, że największy negatywny wpływ na stan zdrowotny drzew *Tilia cordata* Mill. w parkach Poznania miała niewielka odległość parków od centrum miasta oraz bezpośrednia bliskość dwóch arterii komunikacyjnych. Stwierdzono również, że bliskość zabudowań ogrzewanych paliwami kopalnymi, przede wszystkim węglem kamiennym, mogły wpływać negatywnie na stan zdrowotny drzew *Tilia cordata* Mill. na terenie parków Poznania. Wykazano również, że osobniki drzew badanego gatunku z przedziału wiekowego 81–120 lat charakteryzowały się najgorszym stanem zdrowotnym, a najlepszą zdrowotność drzew *Tilia cordata* Mill. stwierdzono w Parku Tysiąclecia Państwa Polskiego.

Słowa kluczowe: tereny zurbanizowane, Poznań, zmienne środowiskowe, modele statystyczne

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PESTICIDE RESIDUES AND ACUTE DIETARY RISK ASSESSMENT IN POLISH RAW FOOD (2005–2013)

POZOSTAŁOŚCI PESTYCYDÓW I OCENA OSTREGO RYZYKA W POLSKIEJ ŻYWNOŚCI POCHODZENIA ROŚLINNEGO (2005–2013)

Abstract: Food safety is very important for consumers. Fruits, vegetables and cereals are not only the major source of vitamins, minerals, fibre and energy, but can also be a source of many pollutants posing health hazards. Pesticides found in food are just examples of harmful substances affecting food safety. The objective of this paper was to assess short-term health risks assessment based on the concentration of pesticide residues found in agricultural products collected from national food control systems during the period 2005–2013 at the Official Pesticide Residue Laboratory in Bialystok in frame of RASFF (Rapid Alert System for Food and Feed) system. During nine-year testing, totally 2021 fruits, vegetables and cereals were sampled from the north-eastern and central part of Poland and analyzed by gas and liquid chromatography and spectroscopic technique for the presence of 188 active substances of pesticides. Contaminations were not detected in 65.3 % of samples, 31.9 % samples contained residues below the maximum residue levels (MRLs), while 2.8 % of tested samples exceeded MRLs. Among 81 RASFF notifications noted, the greatest number of irregularities concerned exceeding the values of MRL – 41, in 27 cases it was found that a pesticide was not used in accordance with the registration of plant protection product. The highest estimated values for short-term exposure were obtained for plum for the dimethoate, and in the group of toddlers it was 94.6 % ARfD (Acute Reference Dose), and in the adult group it was 23.3 % ARfD.

Keywords: Active substances of pesticides, north-eastern Poland, RASFF notification, food safety

One of the most important factors determining human health is a proper diet, which is a prerequisite for our growth, both physical and mental, general well-being. While a wholesome meal is significant to a consumer's health, one should also note the quality of the food eaten. Fruits and vegetables are key components of a healthy diet. They are

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low fat and low energy-dense foods, relatively rich in vitamins, minerals and other bioactive compounds, as well as being a good source of fibre. A high intake of fruits and vegetables in the diet is positively associated with the prevention of cardiovascular disease, cancer, diabetes and osteoporosis. However, fruits, vegetables and cereals are not only the major source of vitamins, minerals, fibre and energy, but can also be a source of many pollutants posing health hazards. Pesticides, heavy metal, and mycotoxins found in food are just a few examples of harmful substances affecting food safety [1–3]. Other hazards include food-poisoning bacteria (including Salmonella) [4–6], but also an inappropriate diet which can lead to overweight, obesity [7]. Data from literature confirm that one of the drawbacks of using plant protection products (p.p.p.) is their potential risk to human health due to the presence of active substances of pesticide residue in fresh food products [8, 9]. Pesticides have been associated with a wide range of ill health symptoms, ranging from short-term headaches and nausea to cancer, reproductive harm, and endocrine disruption [10]. Moreover, extensive or inappropriate use of p.p.p. by farmers can lead to contamination of various ecosystems [11].

In modern times, the issue of the safety and quality of food is a major public concern, and, if neglected, would seriously endanger consumers' health. Food safety remains a key challenge for the European Union (EU) agriculture, especially when, according to Food and Agriculture Organization of the United Nations (FAO), before 2050 the demand for food will have doubled (especially in countries such as India and China) [12].

The Rapid Alert System for Food and Feed (RASFF) is a significant element in managing food safety. Created by the European Commission in accordance with European Parliament Regulation No. 178/2002 [13] on food law, it is meant to provide a quick response about dangerous food substances that fail to meet with safety requirements. RASFF members include: The European Commission (network administration authority), EU member states, European Food Safety Authority (EFSA), EU candidate countries, other countries as well as international organizations. In RASFF system, a member state sets up a national contact point gathering information on food and feed that happen to pose direct or indirect danger to health. The information is then passed on to the European Commission, which immediately notifies other RASFF members [14].

In Poland, procedures and requirements (in accordance with EU regulations) necessary to ensure food safety, are determined by the Act of 25th August, 2006 [15]. Under this act, relevant inspection authorities and food producers are obliged to monitor active substances concentration levels in food, and then to compare the results with the maximum residue levels (MRLs). In aspect of pesticides, to RASFF system samples with residues greater than the maximum residue levels (the residue is from a pesticide that is registered in Poland, but the amount is greater than the MRL set by EFSA), samples with residues of unregistered pesticides (the residue is from a pesticide that is not registered in Poland for any use) and/or "off label" residues (the residue is from a pesticide that is registered for some uses in Poland, but not for the crop on which it was used) are reported. The RASFF system has been in operation in Poland since 2004, and is coordinated by the Chief Sanitary Inspector (GIS). Notifications provided through RASFF may include information on market notifications (two types: alert and information notifications) and border rejections.

The objective of this paper is to evaluate the quality of local raw fruits, vegetables and cereals in aspect of active substances presence on the basis of RASFF notifications made during the period 2005–2013 at the Laboratory of Pesticide Residue of the Plant Protection Institute – National Research Institute in Bialystok and to evaluate on that basis the consumer's risk related to short-term exposure.

Materials and methods

Standards

Pesticides (188 active substances) were obtained from Dr. Ehrenstorfer Laboratory (Germany). Standard stock solutions (purity for all standards >95 %) of various concentrations were prepared in acetone and stored in dark below 4 ^{o}C. The tests covered the determination of active substances of pesticides, from 93 in 2005 to 188 in 2013.

Reagents and chemicals

All reagents used were analytical grade. Acetone, *n*-hexane, diethyl ether, toluene, dichloromethane for pesticides residue analysis, florisil (60–100 mesh) and phosphate buffer pH = 8 were provided by J.T. Baker (Deventer, Holland). Acetonitrile, methanol, hydrochloric acid, sodium hydroxide, potassium hydroxide, zinc acetate dihydrategrade, anhydrous sodium acetate, anhydrous tin (II) chloride, ammonium iron (III) sulfate were purchased from POCH (Gliwice, Poland). Silica gel (230–400 mesh) and N,N-dimethyl-1,4-phenylenediammonium dichloride were obtained from Merck (Darmstadt, Germany). The anhydrous sodium sulfate was purchased from Fluka (Seelze-Hannover, Germany). Sodium sulfide nonahydrate and celite were supplied by Sigma-Aldrich (St. Louis, USA). Before use all sorbents were activated at 600 ^{o}C.

Samples

During 2005–2013, in the framework of the official testing of residues of plant protection products conducted by the Ministry of Agriculture and Rural Development, totally 2021 samples of fruits, vegetables, cereals and oilseeds were analyzed for active substances of pesticides. These samples were collected between May–November by the regional inspectors of Plant Protection and Seed according to a predetermined schedule for a given.

Analytical methods

Sample preparation was done using three techniques (Fig. 1): Multi Residue Method (MRM) and two Single Residue Methods (SRM), fully described in our earlier published work [16, 17, 18, 19]. These methods were validated and accredited in

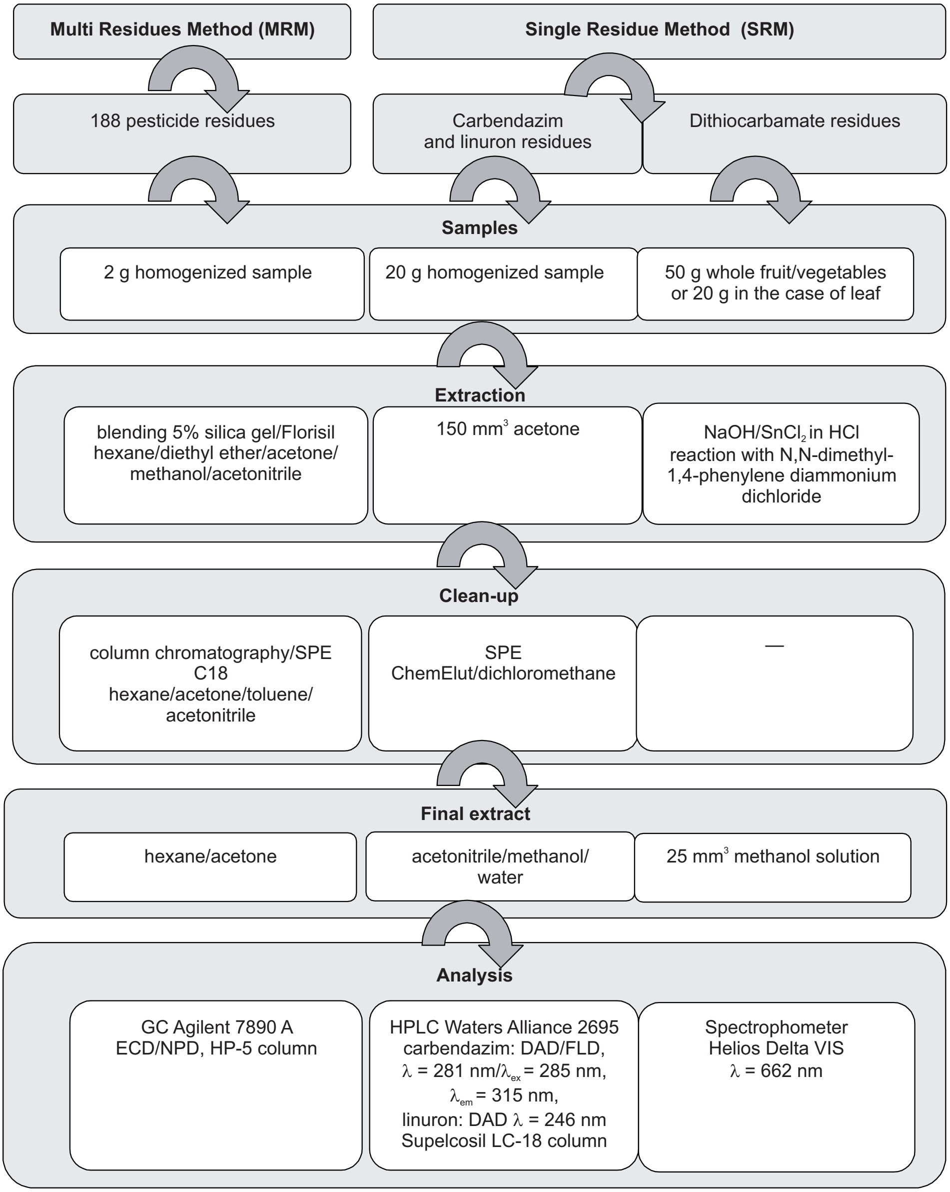

Fig. 1. Scheme of sample preparation procedures
Legend: MSPD – matrix solid phase dispersion; GC – gas chromatography; HPLC – high-performance liquid chromatography; ECD/NPD – electron capture detector/nitrogen phosphorus detector; DAD – diode array detector; FLD – fluorescence detector

accordance with PN-EN ISO/IEC 17025 [20] by the Polish Center of Accreditation, PCA.

Quality check

To be sure about the quality of results, the Laboratory has accreditation PN/EN ISO IEC 17025 and regularly take a part with satisfactory performance in external proficiency assessment schemes in proficiency testing schemes organized and run by the Food Analysis Performance Assessment Scheme (FAPAS; Central Science Laboratory in York) and by the European Commission (University of Almeria). Participation in EC tests is mandatory for all Official Laboratory undertaking the analysis of these commodities for the official controls on pesticide residues, using of validated methods and the employment of suitably qualified persons to carry out analysis.

Risk assessment

Non-compliances related with exceeding of MRLs was assessed in relation to national and EU legislation [21, 22], in the case of detection of active substance of forbidden p.p.p. on the market according to plant protection act [23]. The evaluation was conducted for the general population of consumers (adults) and critical population, children aged from 1.5 to 4 years, as the group most vulnerable to the effects of exposure to active substances of pesticide residues.

Short-term exposure was estimated by comparing single intake of the highest detected residue of plant protection products to a set volume ARfD (Acute Reference Dose).

Short-term exposure was calculated according to the following formula [24]:

$$ESTI = \sum \frac{F \cdot HR \cdot P}{\text{mean\_ weight}}$$

where: $ESTI$ – Estimate of Short-Term Intake;
F – full portion consumption data for the commodity unit;
HR_P – the highest residue level.

The risk assessment of consumer health exposure associated with consumption of crops containing pesticide based on the available epidemiological studies conducted for the two sub-populations in the database of food consumption: the British model, Pesticides Safety Directorate [25], consumption at 97.5 percentile. In Poland there is no complete data for this populations, hence the need to use other available sources. Values of ARfD are elaborated by European Food Safety Authority (EFSA) of EU [26] or Federal Institute for Risk Assessment (BfR), Germany [27].

Results and discussion

In 2005–2013, 2021 crop samples were tested. Contaminations were found in 34.7 % of the samples. 31.9 % samples contained residues below the maximum residue levels (MRLs), while 2.8 % of tested samples exceeded MRLs and in 65.3 % were not detected. Detailed data referring to particular years are shown in Table 1.

Table 1

Occurrence of pesticide residues in samples analyzed during the years 2005–2013

Year	Samples without residues	% to total samples	Samples with detected residues below MRL	% to total samples	Samples with detected residues above MRL	% to total samples
2005	161	8.0	108	5.3	4	0.2
2006	164	8.1	51	2.5	3	0.1
2007	129	6.4	79	3.9	6	0.3
2008	182	9.0	76	3.8	18	0.9
2009	173	8.6	90	4.5	5	0.2
2010	198	9.8	63	3.1	6	0.3
2011	90	4.5	33	1.7	3	0.1
2012	95	4.7	22	1.1	0	0
2013	128	6.3	120	5.9	12	0.6
Total	1320	65.3	644	31.9	57	2.8

During the researched period from among the 81 notifications noted at the Laboratory of Pesticide Residue in Bialystok (Fig. 2), the largest number of notifications was made in the year 2008 – 21. In 2013, seventeen RASFF notifications were made, and it was the second highest score in 9-year period. Year 2012 was the only year when no notifications were recorded.

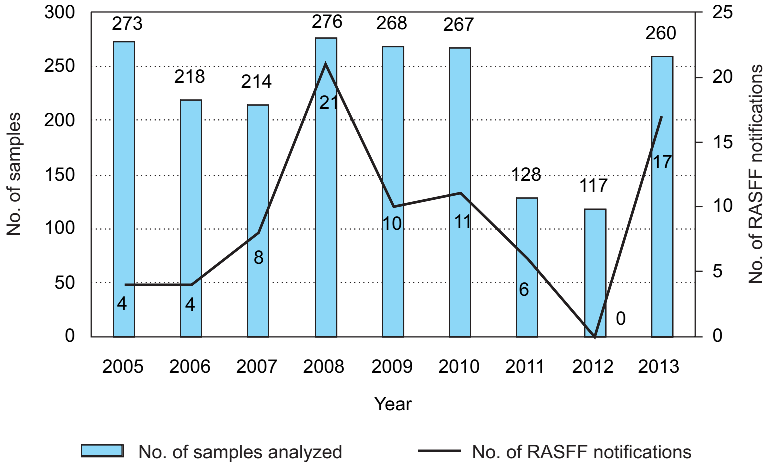

Fig. 2. RASFF notifications in 2005–2013

The greatest number of irregularities concerned exceeding the values of MRL – 41, in 27 cases it was found that a pesticide was not used in accordance with the registration, and in 13 cases simultaneous excess of MRL and the use of non-registered pesticides have occurred.

Data of the National Sanitary Inspectorate had shown that, the National Contact Point in 2013, during the official control in the country 270 RASFF notifications received (in 2012 – 443, in 2011 – 384, in 2010 – 219, in 2009 – 248, in 2008 – 292, in 2007 – 257, in 2006 – 193, in 2005 – 102 notifications) [27]. The number of notifications reported during the official control increased systematically until 2012 (with the exception of the years 2009 and 2010, when a slight decrease was recorded), and then in 2013 the number decreased by ca. 27 %. The decrease in the number of notifications may be indicative of an improving quality of agricultural-food products present in the trade volume within the territory of our country [14] or it may be an isolated occurrence. As follows from RASFF Annual Report [28], Poland sent 120 notifications in 2013, which places it on the 7th position among the notifying entities. The largest number of notifications was sent to the European Commission in 2013 by Contact Points situated in Italy (534 notifications), in Germany (331 notifications), United Kingdom (327 notifications), Netherlands (264 notifications) and France (249 notifications). Petroczi et al [29] revealed, that in the years 2000–2009, 60 % of the RASFF notifications were made by Italy, Germany, the UK and Spain.

The most frequent hazards reported to the RASFF system in north-eastern Poland in 2013 (similarly to the year 2010, 2009, 2008, 2007, 2006, 2005) included fruit contamination (Fig. 3). Only in 2011 more notifications for vegetables were recorded.

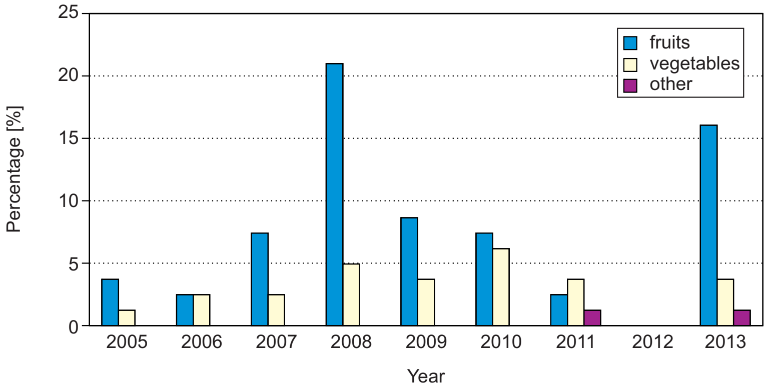

Fig. 3. Number of notifications according to the food products in 2005–2013

Notifications of the fruits constituted 69.1 %, vegetables and cereals, oilseeds were 28.4 % and 6.5 %, respectively. The results another authors confirm that fruits are the group of crops where the producers use chemical p.p.p. most frequently [30, 31]. The largest number of notifications concerned samples of currants (34.6 %) and apples (22.3 %). Currants belong to the group of fruits where exceeding of the MRL [32] and using of the unauthorised chemical p.p.p. were the most frequently detected. The maximum residue level was exceeded in 25 currant samples, including alpha–cypermethrin (two samples: 0.08; 0.1 mg/kg, MRL = 0.05 mg/kg), cypermethrin (three samples: 0.09; 0.14; 0.22 mg/kg, MRL = 0.05 mg/kg), difenoconazole (one sample: 0.43 mg/kg, MRL = 0.05 mg/kg), endosulfan (one sample: 0.28 mg/kg, MRL = 0.05

mg/kg), esfenvalerate (two samples: 0.1; 0.15 mg/kg, MRL = 0.02 mg/kg), fenazaquin (ten samples: 0.03; 0.04; 0.05; 0.09; 0.11; 0.13; 0.19; 0.22; 0.24; 0.25 mg/kg, MRL = 0.01 mg/kg in 2007–2008 and MRL = 0.1 mg/kg in 2009–2013), fenitrothion (four samples: 0.03; 0.02 mg/kg, MRL = 0.01 mg/kg), flusilazole (one sample: 0.05 mg/kg, MRL = 0.02 mg/kg), procymidone (one sample: 0.024 mg/kg, MRL = 0.02 mg/kg) and tolylfluanid (one sample: 0.03 mg/kg, MRL = 0.02 mg/kg). The use of unauthorised products by producers were connected mainly with the lack of appropriate products registered for protection of a given type of crops. For example, from the group of fungicides: flusilazole (1), azoxystrobin (1) and tolylfluanid (1) in currants were detected. From the group of insecticides: fenazaquin (3) and endosulfan (2) were detected. These results confirm problems with the chemical protection of minor crops [33]. Moreover, the large number of notifications concerning apples results, among other factors, from the fact that this type of fruit due to its predominance in consumption is one of the most frequently tested product [34–41].

In total, 30 different active substances of pesticides, belonging to 18 different chemical groups, were found (Table 2).

Table 2

Active substances of pesticides detected in analysed samples
from north-eastern and central Poland

Category	Chemical group	Active substance name	Samples	Range [mg/kg]	Commodity
A/I	Unclassified	Fenazaquin	13	0.030–0.250	Currant, apple
	Organophosphate	Diazinon	8	0.010–0.270	Lettuce, apple, radish, mushroom, pear, carrot
		Fenitrothion	7	0.020–0.060	Currant, apple
		Chlorpyrifos	6	0.010–0.560	Apple, broccoli, carrot, parsnip
		Dimethoate	6	0.020–0.320	Apple, plum, pear, cucumber
		Phosalone	3	0.030–0.250	Apple
		Pirimiphos-methyl	1	0.240	Rape
	Organochlorine	Endosulfan	2	0.030–0.280	Currant
		DDT	1	0.093	Lupin
	Pyrethroid	Cypermethrin	3	0.090–0.220	Currant
		Alpha-cypermethrin	2	0.080–0.100	Currant
		Esfenvalerate	2	0.100–0.150	Currant
		Bifenthrin	1	0.150	Mushroom
F	Triazole	Flusilazole	7	0.010–0.290	Currant, apple
		Difenoconazole	2	0.270–0.430	Gooseberry, currant
		Tebuconazole	1	0.070	Chinese cabbage
	Dicarboximide	Procymidone	5	0.020–0.570	Currant, lettuce, strawberry, tomato
	Anilinopyrimidine	Pyrimethanil	4	0.030–0.200	Apple, chinese cabbage

Table 2 contd.

Category	Chemical group	Active substance name	Samples	Range [mg/kg]	Commodity
F	Strobilurin	Azoxystrobin	3	0.050–0.060	Currant, cucumber, parsley root
	Carboxamide	Boscalid	3	0.060–0.230	Apple, pear, sour cherry
	Chloronitrile	Chlorothalonil	3	0.060–8.470	Tomato, chinese cabbage, parsley root
	Benzimidazole	Carbendazim	2	0.010–0.020	Mushroom
	Sulphamide	Tolylfluanid	2	0.030–0.490	Strawberry, currant
		Dichlofluanid	1	18.680	Lettuce
	Phthalimide	Captan	1	0.350	Sour cherry
	Anilinopyrimidine	Cyprodinil	1	0.090	Apple
	Morpholine	Dimethomorph	1	1.040	Tomato
	Hydroxyanilide	Fenhexamid	1	0.220	Sour cherry
	Strobilurin	Trifloxystrobin	1	0.020	Sour cherry
H	Dinitroaniline	Trifluralin	1	0.040	Carrot

I – Insecticide; F – Fungicide; H – Herbicide; A – Acaricide.

In our study, the most frequently detected group of active substances were insecticides, which comprised 58.3 % of all detections (fenazaquin, diazinon, fenitrothion, chlorpyrifos, dimethoate, phosalone, pirimiphos–methyl, endosulfan, DDT, cypermethrin, alpha-cypermethrin, esfenvalerate, bifenthrin). The largest number of notifications referred to the detection of fenazaquin (13) in samples of currants and apples. Fenazaquin is a non-systemic pesticide used to control mites and other related pests in fruits, vegetables and tea [42]. In turn, 8 concerned the detection of diazinon in samples of lettuce, apples, pears, carrots, mushrooms, radishes, which is a non-systemic organophosphate insecticide used to control pests in fruits, vegetables, ornamentals and other crops [43]. Flusilazole and fenitrothion were identified in 7 samples of currants and apples. Flusilazole is a systemic fungicide used to control fungal diseases in cereals, fruits, vegetables, and nuts [41]; fenitrothion is a non-systemic insecticide used to control various pests in fruit and other crops.

Table 3 shows details for each active substances of pesticides and groups with the same mode of action [44]. These data present carcinogenic properties of captan, procymidone and suggest that thirteen other compounds (bifenthrin, cypermethrin, dimethoate, DDT, endosulfan, boscalid, carbendazim, chlorothalonil, difenoconazole, flusilazole, tebuconazole, tolylfluanid, trifluralin) may have possible carcinogen effect.

Short-term exposure is shown in Table 4. The highest values of short-term exposure were obtained for plum, and for the group of toddlers it was 94.6 % ARfD, and for the adult group it was 23.3 % ARfD. In both cases these values did not exceed the acceptable 100 % threshold. In case of consumption other products, the short-term exposure (ARfD) didn't exceed: 60 % for the group of toddlers and 15 % for the adults.

Table 3

Active substances of pesticides found in samples with corresponding health effects

Substance group	Pesticide	Mode of action	Carcinogen	Mutagen	Endocrine disruptor	Reproduction/ development effects	Acetyl cholinesterazy inhibitor	Neurotoxicant	Respiratory tract irritant	Skin irritant	Eye irritant
Acaricides/ Insecticides											
Pyrethroid	Alpha-cyprmethrin	Non-systemic with contact and stomach action. Sodium channel modulator.	—	—	?	—	X	—	V	V	X
	Bifenthrin	Contact and stomach action with some residual effect. Sodium channel modulator.	?	?	V	?	X	V	—	X	X
	Cypermethrin	Non-systemic with contact and stomach action. Sodium channel modulator.	?	X	?	?	X	X	V	V	V
	Esfenvalerate	Contact and stomach action. Sodium channel modulator.	X	X	?	?	X	X	—	X	X
Organophosphate	Chlorpyrifos	Non-systemic with contact and stomach action. Acetylcholinesterase (AChE) inhibitor.	X	X	?	V	V	V	X	?	?
	Diazinon	Non-systemic with respiratory. Contact and stomach action. Acetylcholinesterase (AChE) inhibitor.	X	?	V	?	V	V	V	V	V
	Dimethoate	Systemic with contact and stomach action. Acetylcholinesterase (AChE) inhibitor.	?	X	?	V	V	X	—	X	V

Table 3 contd.

Substance group	Pesticide	Mode of action	Carcinogen	Mutagen	Endocrine disruptor	Reproduction/ development effects	Acetyl cholinesterazy inhibitor	Neurotoxicant	Respiratory tract irritant	Skin irritant	Eye irritant
Organophosphate	Fenitrothion	Non-systemic. Broad spectrum with contact and stomach action. Acetylcholinesterase (AChE) inhibitor.	X	X	V	—	V	X	—	V	X
	Phosalone	Non-systemic with contact and stomach action. Acetylcholinesterase (AChE) inhibitor.	X	—	—	—	V	V	V	V	V
	Pirimiphos-methyl	Broad-spectrum with contact and respiratory action. Acetylcholinesterase (AChE) inhibitor.	X	—	—	—	V	—	V	V	?
Organochlorine	DDT	Non-systemic stomach and contact action. Sodium channel modulator.	?	V	V	X	V	?	X	X	—
	Endosulfan	Non-systemic with contact and stomach action, acts as a non-competitive GABA antagonist.	?	V	?	—	X	V	—	—	—
Unclassified	Fenazaquin	A mitochondrial electron transport inhibitor with contact action.	X	—	X	?	X	—	V	X	X
Fungicides											
Anilinopyrimidine	Cyprodinil	Systemic. Absorbed through foliage. Inhibits protein synthesis.	X	X	—	?	X	X	V	V	V
	Pyrimathanil	Protective action with some curative properties.	X	—	?	X	X	X	—	X	?

Table 3 contd.

Substance group	Pesticide	Mode of action	Carcinogen	Mutagen	Endocrine disruptor	Reproduction/ development effects	Acetyl cholinesterazy inhibitor	Neurotoxicant	Respiratory tract irritant	Skin irritant	Eye irritant
Benzimidazole	Carbendazim	Systemic with curative and protectant activity. Inhibition of mitosis and cell division.	?	—	?	V	X	X	X	X	X
Carboxamide	Boscalid	Protectant. Foliar absorption. Translocates. Inhibits spore germination and germ tube elongation.	?	—	X	?	X	X	X	X	?
Chloronitrile	Chlorothalonil	Non-systemic. Broad spectrum. Foliar action with some protectant properties. Acts by preventing spore germination and zoospore motility.	?	X	X	—	X	X	V	V	V
Dicarboximide	Procymidone	Systemic with protective and curative properties.	V	—	V	V	X	—	?	X	X
Hydroxyanilide	Fenhexamid	Foliar applied with protective action. Disrupts membrane function. Inhibits spore germination.	X	—	?	X	X	X	X	X	—
Morpholine	Dimethomorph	Systemic with good protective activity. Lipid synthesis inhibitor.	X	X	—	?	X	X	V	V	V
Phthalimide	Captan	Non-systemic with protective and curative action.	V	X	X	—	X	X	—	V	V
Sulphamide	Dichlofluanid	Foliar with protective action	—	—	—	—	X	—	?	?	?

Table 3 contd.

Substance group	Pesticide	Mode of action	Carcinogen	Mutagen	Endocrine disruptor	Reproduction/ development effects	Acetyl cholinesterazy inhibitor	Neurotoxicant	Respiratory tract irritant	Skin irritant	Eye irritant
Sulphamide	Tolylfluanid	Broad spectrum. Multi-site with protective action.	?	—	—	X	X	X	—	V	V
Strobilurin	Azoxystrobin	Systemic translaminar and protectant action having additional curative and eradicant properties. Respiration inhibitor (QoL fungicide).	X	—	—	?	X	X	—	V	V
	Trifloxystrobin	Broad spectrum with preventative and curative action. Respiration inhibitor. (QoL fungicide)	X	—	—	V	X	X	—	V	X
Triazole	Difenoconazole	Systemic with preventative and curative action. Disrupts membrane function - inhibition of demethylation during ergosterol synthesis.	?	—	—	?	X	X	X	V	V
	Flusilazole	Broad spectrum. Systemic with protective and curative action	?	—	—	V	X	X	?	?	?
	Tebuconazole	Systemic with protective. Curative and eradicant action. Disrupts membrane function.	?	—	—	V	X	X	X	X	V
Herbicides											
Dinitroaniline	Trifluralin	Selective. Inhibition of mitosis and cell division.	?	X	V	V	X	—	V	X	X

V – Yes, known to cause a problem; X – No, known not to cause a problem; ? – Possibly, status not identified; – No data.

Table 4

Estimation of short-term (acute) dietary consumer's exposure (2005–2013)

Crop	Active substance	HR [mg/kg]	MRL [mg/kg]	Times exceeded MRL	ARfD* [mg/kg b.w.]	Source	Adults		Children	
							Intake [mg/kg b.w.]	% ARfD	Intake [mg/kg b.w.]	% ARfD
Currant	Alpha-cypermethrin	0.10	0.05	2	0.04	Dir 04/58	0.00016	0.4	0.00036	0.9
Mushroom	Bifenthrin	0.15	0.05	3	0.03	EFSA 11	0.00024	0.8	0.00044	1.5
Carrot	Chlorpyrifos	0.56	0.10	5.6	0.1	Dir 05/75	0.00485	4.9	0.02201	22.0
Tomato	Chlorothalonil	8.47	2.00	4.2	0.6	SCoFCAH Sept 06	0.08838	14.7	0.35077	58.5
Currant	Cypermethrin	0.22	0.05	4.4	0.2	Dir 05/53	0.00035	0.2	0.00079	0.4
Apple	Cyprodinil	0.09	0.05	1.8	0.03	Dir 06/64	0.00135	4.5	0.00648	21.6
Lubin	DDT	0.09	0.05	1.9	Not appl.	JMPR 2000	—	—	—	—
Lettuce	Diazinon	0.27	0.02	13.5	0.025	EFSA 06	0.00266	10.7	0.00326	13.0
Lettuce	Dichlofluanid	18.68	5.00	3.7	Not appl.	—	—	—	—	—
Currant	Difenoconazole	0.43	0.05	8.6	0.16	Dir 08/69	0.00068	0.4	0.00155	1.0
Plum	Dimethoate	0.32	0.02	16	0.01	EFSA 2013	0.00233	23.3	0.00946	94.6
Tomato	Dimethomorph	1.04	0.50	2.1	0.6	Dir 07/25	0.01085	1.8	0.04307	7.2
Tomato	Endosulfan	0.28	0.05	5.6	0.02	JMPR 2006	0.00292	14.6	0.01160	58.0
Currant	Esfenvalerate	0.15	0.02	7.5	0.05	Dir 00/67	0.00024	0.5	0.00054	1.1
Currant	Fenazaquin	0.250	0.10	2.5	0.1	EFSA 2013	0.00039	0.4	0.00090	0.9

Table 3 contd.

Crop	Active substance	HR [mg/kg]	MRL [mg/kg]	Times exceeded MRL	ARfD* [mg/kg b.w.]	Source	Adults		Children	
							Intake [mg/kg b.w.]	% ARfD	Intake [mg/kg b.w.]	% ARfD
Currant	Fenitrothion	0.06	0.01	6	0.013	EFSA 06	0.00009	0.7	0.00022	1.7
Currant	Flusilazole	0.29	0.02	14.5	0.005	Dir 06/133	0.00046	0.9	0.00104	2.1
Apple	Phosalone	0.25	0.05	5	0.1	EFSA 06	0.00374	3.7	0.01801	18.0
Apple	Pyrimethanil	0.20	0.01	20	Not appl.	Dir 06/74	—	—	—	—
Rape	Pirimiphos-methyl	0.24	0.05	4.8	0.15	EFSA 05	0.00144	1.0	0.00324	2.2
Currant	Procymidone	0.57	0.02	28.5	0.012	DAR 07	0.00090	7.5	0.00205	17.1
Strawberry	Tolylfluanid	0.49	0.02	24.5	0.25	Dir 06/06	0.00129	0.5	0.00240	1.0

HR – Highest residue, MRL – Maximum Residue Limit, ARfD – Acute Reference Dose, b.w. – body weight; * ARfD values are derived from the pesticide database [45].

All RASFF notifications made during the period 2005–2013 at the Laboratory of Pesticide Residue in Bialystok had the character of information notifications. The estimated health risk assessment was acceptable, therefore notifications were not passed on to the European Commission.

Conclusions

Presented research concerns the evaluation of quality of local raw fruits, vegetables cereals and oilseeds in aspect of active substances presence on the basis of RASFF notifications made during the period 2005–2013. The estimated that acute exposure was highest for the dimethoate, however, it was lower than 100 % ARfD. No products were found in which consumption may have negative health effects. The present study shows that although fruits and vegetables from the region of Poland contain many contaminations, their consumption does not pose a danger to the health of adults and children. Nevertheless, studies on pesticide residues should still be developed and should include more and more active substances and various species of vegetables, fruits, cereals and processed goods of plant origin.

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POZOSTAŁOŚCI PESTYCYDÓW I OCENA OSTREGO RYZYKA W POLSKIEJ ŻYWNOŚCI POCHODZENIA ROŚLINNEGO (2005–2013)

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Abstrakt: Bezpieczeństwo żywności jest bardzo ważne dla konsumentów. Owoce, warzywa i zboża są nie tylko ważnym źródłem witamin, minerałów, błonnika i energii, ale również mogą być źródłem wielu zanieczyszczeń mogących stanowić ryzyko dla zdrowia. Pestycydy znajdujące się w żywności to tylko przykłady szkodliwych substancji wpływających na bezpieczeństwo żywności. Celem niniejszej pracy była ocena krótkoterminowego zagrożenia zdrowia na podstawie stężenia pozostałości pestycydów w płodach rolnych pobranych w ramach urzędowej kontroli w okresie 2005–2013 w ramach systemu RASFF (System Wczesnego Ostrzegania o Niebezpiecznej Żywności i Paszach). W dziewięcioletnim okresie badań łącznie 2021 próbek owoców, warzyw i zbóż pobrano z północno-wschodniej i środkowej części Polski i analizowano pod kątem obecności 188 substancji czynnych pestycydów techniką chromatografii gazowej, cieczowej i spektrofotometryczną. Wolnych od zanieczyszczeń było 65,3 % próbek, 31,9 % próbek zawierało pozostałości poniżej, a w 2,8 % powyżej najwyższych dopuszczalnych poziomów (NDP). Spośród 81 powiadomień informacyjnych RASFF, najwięcej nieprawidłowości dotyczyło przekroczenia wartości NDP – 41, w 27 przypadkach stwierdzono, że pestycyd nie był używany zgodnie z rejestracją środka ochrony roślin. Najwyższe oszacowane wartości krótkotrwałego narażenia zdrowia uzyskano dla śliwki dla dimetoatu, w grupie małych dzieci – 94,6 % ARfD (Ostra Dawka Referencyjna) i dorosłych – 23,3 % ARfD.

Słowa kluczowe: Substancje aktywne pestycydów, północno-wschodnia Polska, powiadomienia informacyjne RASFF, bezpieczeństwo żywności

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MODELING STUDIES OF HYDRAULIC EFFICIENCY OF COMPACTED WASTE LANDFILL CLAY LINER

MODELOWANIE FUNKCJONOWANIA PRZESŁONY SKŁADOWISKA ODPADÓW WYKONANEJ Z ZAGĘSZCZONEGO GRUNTU ILASTEGO

Abstract: Compacted clay materials are commonly used worldwide as sealing materials to prevent migration of anthropogenic pollutants from municipal landfill cells to the environment. Such clay barriers known as liners are sealing the top, sides and bottom of the landfill. They limit water infiltration to waste body and leachate seepage, usually with the required saturated hydraulic conductivity lower than $1.0 \cdot 10^{-9}$ m $\cdot$ s^{-1}. The value of resultant hydraulic conductivity of compacted clay liners and their sustainability affected by swelling and shrinking processes are related to molding water content. This paper presents results of studies concerning the influence of molding water content on saturated hydraulic conductivity and shrinkage/swelling properties of selected compacted clay materials as well as hydraulic properties of the top sealing liner, constructed according to the actual standards of compacted clay material. Our studies covered field and laboratory measurements as well as numerical modeling. Permeability and water retention characteristics of the clays were determined during field and laboratory tests. Saturated hydraulic conductivity under the natural in situ conditions was measured by BAT probe, GeoNordic. Hydraulic conductivity of the homogenized compacted clays was tested in the laboratory by Humboldt Mfg. Co. permeameters for compacted soils, according to ASTM D5856. Water retention characteristics of the compacted clays in the range of 0–15 bar pore water tension were determined by application of sand box and pressure chamber methods. The numerical assessment of the hydraulic efficiency of the clay liner was performed for the 2012 hydrologic year for a selected section of landfill top cover constructed in Rastorf, Germany, adjusted to Polish standards. The numerical calculations were performed in FEFLOW, DHI-WASY modeling software.

Keywords: clay materials, mineral liners, hydraulic conductivity, numerical modeling

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Introduction

Landfilling of municipal wastes and the subsequent possible migration of numerous pollutants to soil and water, especially by leachate seepage, pose a significant threat to the environment. Generation of leachate is usually triggered by infiltration of surface water, from precipitation and snow cover melting, which can enter the wastes body. Thus, the possible negative environmental impact of landfills depends on the efficiency of limiting the pollution by the applied techniques of landfill sealing [1]. The special barriers, known as liners, based on natural and geosynthetic materials prevent surface water infiltration and leachate migration to soil-water environment. One of the most popular and durable solution known and applied worldwide are compacted mineral clay liners meeting the requirements of the local standards [2, 3]. These barriers are constructed of natural clays of permeability capable to meet the required value of hydraulic conductivity [4], which in the European Union should be lower than $1.0 \cdot 10^{-9}$ $m \cdot s^{-1}$. The saturated hydraulic conductivity of homogenized clays used as a liner construction material under natural conditions may be higher than the above value [5, 6] so the application of compaction is usually required. The compaction, decreasing the porosity of porous material, increases its resistance to water flow, significantly reducing the saturated hydraulic conductivity of the material [7]. The degree of reduction, however, depends on the applied molding water content of the clay. Thus, the molding water content becomes one of the most important factors influencing the hydraulic characteristics of the compacted clay liner [8–12].

On the other hand, molding water content affects also the swelling and shrinking properties of clays, influencing the sustainability of the liner [13–15]. Higher shrinking potential of compacted clays results in a significant risk of liner cracking, and thus, an increase of its permeability. The possible increased permeability of dried clay liners, additionally cracked when dewatered, significantly reduced the sealing capabilities and sustainability of the clay liner. The above issue is crucial in case of top liners where, due to a liner construction and its saturation affected by atmospheric conditions (*eg* precipitation, temperature, moisture). Actual Polish standards [2] require that the clay sealing layer of liner, of saturated hydraulic conductivity lower than $1.0 \cdot 10^{-9}$ $m \cdot s^{-1}$, and top recultivation layer should be separated by the sand drainage layer of saturated hydraulic conductivity greater than $1.0 \cdot 10^{-4}$ $m \cdot s^{-1}$. This feature, combined with possible significant inclination of layers' slope may trigger increased lateral flow and outflow of infiltration water and reduce the possibilities of wetting or rewatering of dried clay sealing layer.

This paper presents an attempt of determination of the effects of soil molding water content on its saturated conductivity, shrinking and swelling potentials and finally the hydraulic properties of the top sealing liner, constructed of tested clay according to the actual standards.

Materials and methods

Our research covered: *i*) determination of the general characteristics of the tested material, including its particle size distribution, particle density, bulk density and field, *in situ* saturated hydraulic conductivity, *ii*) measurement of saturated hydraulic conductivity for soil compacted at various water contents, *iii*) determination of soil's water retention characteristics after compaction, *iv*) measurement of swelling and shrinkage potential of tested soil, *v*) numerical modeling of infiltration process for clay liner allowing to assess its hydraulic efficiency for all applied molding water contents.

The presented studies were focused on mineral clay material sampled in Lazek Ordynacki, approx. 90 km south of Lublin, Poland.

The particle size distribution of the soil was determined by the standard sedimentation method according to PN-B-04481:1988 [16], solid particle density was measured in le Chatelier flask and air pycnometer according to Langer by Eijkelkamp, The Netherlands. Gravimetric water content was obtained by the standard weight method according to ASTM C566-13 [17]. The saturated hydraulic conductivity of the tested soil under natural, undisturbed conditions was measured by the field permeameter for fine grained soils GeoN by Geo Nordic, Stockholm, Sweden. Laboratory measurements of saturated conductivity of the soil compacted at various molding water contents were performed in the permeameters for compacted soils by Humboldt Mfg. Co, USA. The H-4145 compaction permeameters and the falling water head method of measurements, meeting requirements of ASTM D5856-95 [18], were applied to our studies. The soil was compacted, at different molding water contents, according to PN-B-04481:1988 [16].

The following values of molding water contents (by weight) were applied during our laboratory studies: 0.14, 0.17, 0.19, 0.21, 0.22 and 0.23 $\text{kg} \cdot \text{kg}^{-1}$. Water retention capabilities of the compacted clay material were tested in pore water pressure range 0–15 bar by the standard sand box (IMUZ, Lublin, Poland) and pressure chambers with ceramic plates by Soil Moisture, Santa Barbara, USA. The retention characteristics were determined for the following values of pressure: 1, 2, 5, 7, 10, 50, 100, 500, 1000 and 1500 kPa.

Numerical modeling of hydraulic efficiency of a mineral liner constructed of the compacted clay material was performed by FEFLOW, WASY-DHI, Germany modeling software. The developed two dimensional model represented a 10 m wide section of mineral liner of 2 m thickness, required by the actual Polish and European standards [2, 3], consisting of three layers: clay sealing layer of 0.5 m thickness, sand drainage layer of 0.5 m and soil recultivation layer of thickness equal to 1.0 m. The applied slope shape reflected morphology of the selected part of liner in Rastorf, Germany. Top surface of modeled liner was assumed as covered by perennial grass mixture. The prepared model consisted of 5965 nodes and 11549 elements. The developed model was presented in Fig 1.

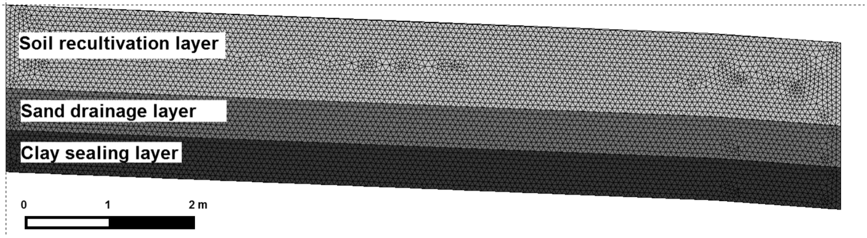

Fig. 1. Developed model of the selected section of municipal landfill top liner

Numerical calculations of the two dimensional water flow in FEFLOW were based on standard forms of Darcy's and Richards' equations [19–21]:

$$\boldsymbol{q}_i = -\boldsymbol{K}_{ij} \frac{\partial h}{\partial x_j}$$

$$\frac{\partial h}{\partial t} = -\frac{\partial \boldsymbol{q}_i}{\partial x_i} \mp Q$$

where: $\boldsymbol{q}_i$ – groundwater flux vector $[\mathrm{m} \cdot \mathrm{s}^{-1}]$,
h – hydraulic pressure head [m],
t – time [s],
$\boldsymbol{K}_{ij}$ – hydraulic conductivity tensor, i, j = 1, 2 $[\mathrm{m} \cdot \mathrm{s}^{-1}]$,
Q – sink or source term $[\mathrm{s}^{-1}]$.

Mathematical description of water retention curve assumed to our simulations was presented by van Genuchten [22]:

$$\theta = \frac{\theta_s - \theta_r}{[1 + (Ah)^n]^m} + \theta_r$$

where: θ_s – saturated volumetric water content $[\mathrm{m}^3 \cdot \mathrm{m}^{-3}]$,
θ_r – residual volumetric water content $[\mathrm{m}^3 \cdot \mathrm{m}^{-3}]$, $\theta_r = 0$ $[\mathrm{m}^3 \cdot \mathrm{m}^{-3}]$,
h – pressure head [m],
A – fitting parameter $[\mathrm{m}^{-1}]$,
n, m – fitting parameters: $m = 1 - n^{-1}$.

Hydraulic conductivity of unsaturated soils K was calculated in the presented model according to van Genuchten's formula [22]:

$$K = K_s S_e^l \left[1 - (1 - S_e^{\frac{1}{m}})^m \right]^2$$

where: K_s – saturated conductivity $[\mathrm{m} \cdot \mathrm{s}^{-1}]$,
l – fitting parameter: $l = 0.5$ [22],
S_e – dimensionless effective saturation defined as:

$$S_e = \frac{\theta - \theta_r}{\theta_s - \theta_r}.$$

Characteristics of sand and recultivation layer assumed to modeling are presented in Table 1. The isotropic hydraulic characteristics of clay and sand soil were assumed to our calculations due to the developed small scale model [23].

Table 1

Soil characteristics for drainage and cultivation layers assumed to modeling

Parameter	Recultivation layer	Sand drainage
Saturated hydraulic conductivity [$\mathrm{m \cdot s^{-1}}$]	$0.02 \cdot 10^{-4}$	$2.0 \cdot 10^{-4}$
Saturated water content θ_s [$\mathrm{m^3 \cdot m^{-3}}$]	0.29	0.37
Residual water content θ_r [$\mathrm{m^3 \cdot m^{-3}}$]	0	0.11
Water retention curve parameter A [$\mathrm{m^{-1}}$]	7.65	2.30
Water retention curve parameter n [-]	1.10	7.70
Anisotropy ratio α [-]	0.17	1
Anisotropy rotation angle ϕ [deg]	90	0

Numerical modeling of water infiltration through the mineral liner required assumption of the necessary initial and boundary conditions. The initial condition was assumed as 90 % liner's soil saturation, $S = 0.9$. The bottom boundary condition was assumed as the constant gradient type Neumann condition of value equal to saturated hydraulic conductivity of the soil in sealing layer. Such a boundary condition reflects the undisturbed free water drainage, *ie* gravitational seepage to the lower domain.

The Neumann type top boundary condition assigned to upper limit of the model reflected water flux entering and leaving the modeled domain. The daily values of water flux were based on measured and calculated daily precipitation, interception, evapotranspiration and surface runoff for municipal landfill in Rastorf, Germany for 2012 hydrologic year [24]. Daily precipitation and runoff were measured by the local weather station and system of surface runoff measurement [24]. Measured values of daily precipitation were corrected, in order to exclude the series of measurement errors of the weather station (*eg* evaporation and wind loss), in accordance to Richter's correction method [25]. Reference daily evapotranspiration was calculated according to the standard Penman-Monteith formula [26, 27], basing on measured weather data and assumed data. Plant cover data (LAI, leaf area index) and assessment of daily interception were performed according to Mitchell et al [28] and Hoyningen-Huene formula [29].

The developed top boundary condition is presented in Fig. 2. The values of daily water flux through the top boundary of modeled domain were obtained by the following formula [24]:

$$q = -P_{\mathrm{corr}} + EV_a + I + q_{\mathrm{runoff}}$$

where: q – daily water flux [$\mathrm{mm \cdot day^{-1}}$],
P_{corr} – corrected daily precipitation [$\mathrm{mm \cdot day^{-1}}$],
EV_a – actual daily evapotranspiration [$\mathrm{mm \cdot day^{-1}}$],
I – daily interception [$\mathrm{mm \cdot day^{-1}}$],
q_{runoff} – daily surface runoff [$\mathrm{mm \cdot day^{-1}}$].

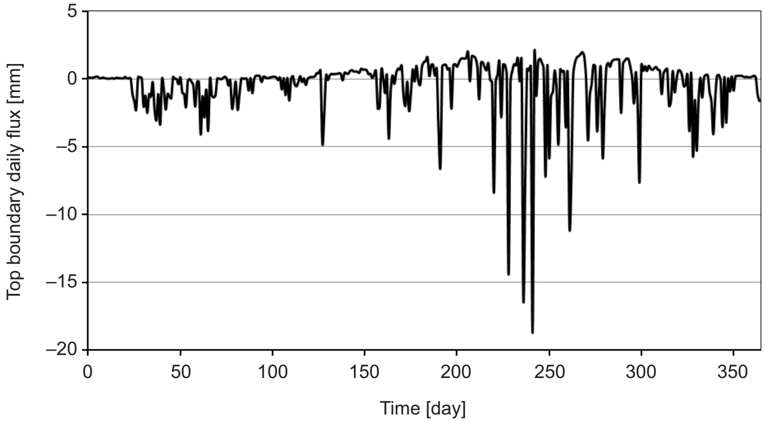

Fig. 2. Assumed top boundary condition, negative values mean infiltration, positive evapotranspiration, based on [25]

Results and discussion

The basic characteristics of sampled clay are presented in Table 2. The tested soil texture class was recognized as silty clay.

The natural, measured in situ hydraulic conductivity of tested soil, lower than $1 \cdot 10^{-9}$ $m \cdot s^{-1}$ meets requirements of the actual Polish and European standards [2, 3] for sealing layers of municipal landfill cells.

Table 2

Basic characteristics of the clay material sampled in Lazek Ordynacki, Poland

Particle fraction name	Sand [%]	4.5
	Silt [%]	51
	Clay [%]	44.5
Solid particle density [$Mg \cdot m^{-3}$]		2.61
Bulk density [$Mg \cdot m^{-3}$]		1.69
Saturated hydraulic conductivity [$m \cdot s^{-1}$]		$1.37 \cdot 10^{-10}$

The results of saturated hydraulic conductivity measurements as well as bulk density, and water retention characteristics according to van Genuchten model for the applied molding water contents are presented in Table 3, Fig. 3 and Fig. 4.

The results presented in Table 3 and in Fig. 3 show a clear decrease of saturated hydraulic conductivity of clay resulting from the increase of molding water content. In most tested cases of compaction at 0.17, 0.19, 0.21, 0.22 and 0.23 $kg \cdot kg^{-1}$ water content allowed to achieve the values of saturated hydraulic conductivity of clay sealing layer lower than required by the standards [2, 3]. The obtained values of K_s are one or even two orders of magnitude lower than the required. However, in case of molding

Table 3

Saturated hydraulic conductivities, bulk densities and water retention parameters of the soil dependently on molding water content

Parameter	Molding water content [kg · kg^{-1}]					
	0.14	0.17	0.19	0.21	0.22	0.23
Saturated hydraulic conductivity [m · s^{-1}]	$3.94 \cdot 10^{-9}$	$1.00 \cdot 10^{-10}$	$7.33 \cdot 10^{-10}$	$3.69 \cdot 10^{-11}$	$3.28 \cdot 10^{-11}$	$3.21 \cdot 10^{-11}$
Bulk density after compaction [Mg · m^{-3}]	1.60	1.66	1.70	1.71	1.71	1.7
Bulk density after swelling [Mg · m^{-3}]	1.45	1.52	1.59	1.63	1.62	1.60
Bulk density after shrinkage [Mg · m^{-3}]	1.80	1.86	1.97	1.93	1.96	2.02
Saturated water content θ_s [m^3 · m^{-3}]	0.388	0.365	0.350	0.346	0.346	0.350
Water retention curve parameter A [m^{-1}]	0.569	0.105	0.928	0.675	0.849	0.100
Water retention curve parameter n [-]	1.118	1.197	1.123	1.116	1.113	1.155

water content equal to 0.14 kg · kg^{-1}, the measured saturated hydraulic conductivity of $3.94 \cdot 10^{-9}$ m · s^{-1} was higher than allowed by the actual Polish and European Union regulations [2, 3].

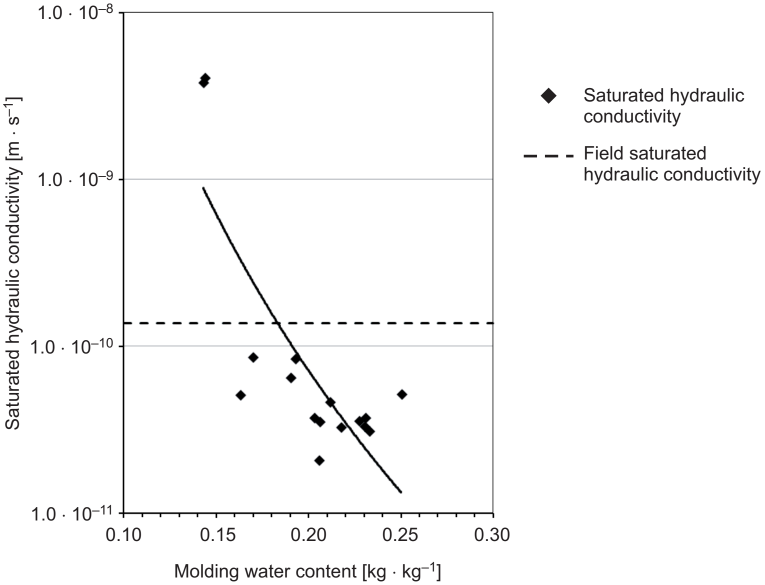

Fig. 3. Saturated hydraulic conductivity of clay material compacted at different water contents

The observed bulk densities of compacted clay, presented in Fig. 4, show that the maximum value of bulk density, identifying the highest possible degree of compaction, was achieved for molding water content of 0.21 kg · kg^{-1}. The highest swelling potential (difference between soil bulk density and bulk density after swelling) equal to 0.16 Mg · m^{-3} was observed for the lowest molding water content applied. On the other hand, the highest shrinkage potential equal to 0.32 Mg · m^{-3} was noted for the highest molding water content applied. Taking into account that high shrinkage potential may trigger cracking which significantly increases hydraulic conductivity of soil, it should be suggested that compaction of clay materials should be performed on the left, "dry", side of Proctor curve. In our case, molding water content between 0.17 and 0.21 kg · kg^{-1} seems to be suitable.

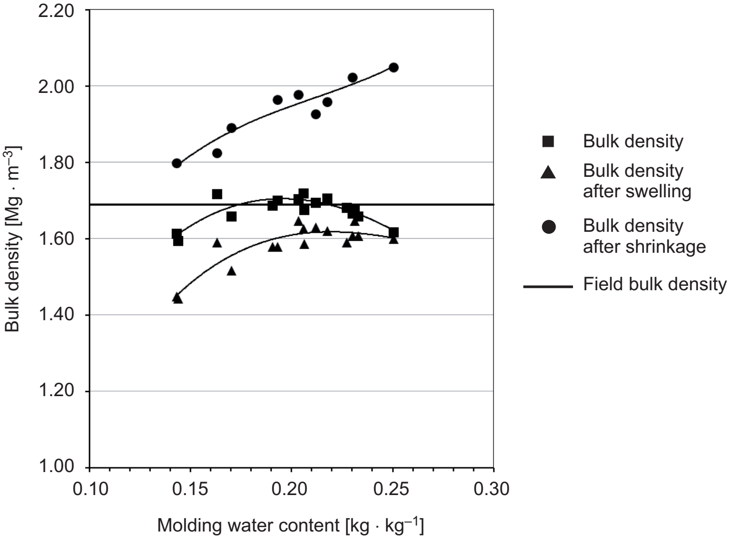

Fig. 4. Bulk density of the clay compacted at various molding water contents

The results of numerical calculations of water seepage through a 10.0 m section of liner utilizing clay compacted at various molding water contents as sealing layer are presented in Fig. 5. The results presented in Fig. 5 show that hydraulic properties of the mineral clay liner as a barrier for pollutants propagation, made of the compacted clay, directly depend on the applied molding water content. The lower the molding water content, the higher saturated hydraulic conductivity and the higher infiltration rate for the same upper boundary condition. The observed calculated decrease of unit yearly seepage volume per 1 m^2 was from 5.41 · 10^{-3} m^3 to 1.8 · 10^{-5} m^3. Fig. 5 shows also that there is no significant difference in sealing capabilities after reaching the maximum bulk density during the compaction process.

Results of our numerical calculations show that seepage rate through the sealing liner is significantly limited due to scarce permeability of compacted clay and construction of the tested liner resulting from actual requirements of Polish standards. The studied layer

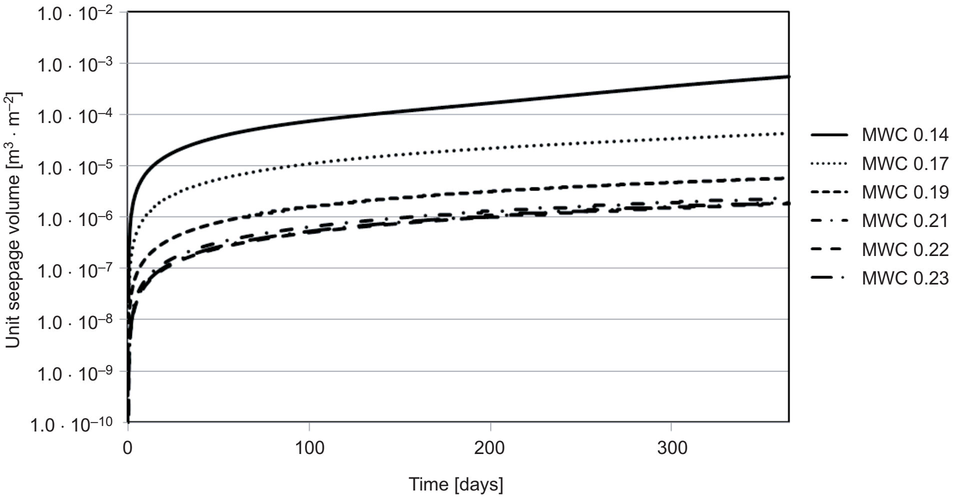

Fig. 5. Calculated yearly cumulative volume of seepage through the bottom boundary of mineral liner made of the clay compacted at different water contents (MWC)

composition, meeting the biding law regulations, assumed the sand drainage layer of thickness 0.5 m located above the compacted clay layer. Thus, two adjacent liner layers were made of materials of a very high difference in permeability, $2 \cdot 10^{-4}$ versus 10^{-9} – 10^{-11} $\text{m} \cdot \text{s}^{-1}$. In this case, the significant lateral fluxes, above the top boundary of sealing layer are possible, which was also observed in our modeling results. Figure 6 shows contour plots of saturation degree and module of velocity vector, together with velocities vector lines for an exemplary time step for 0.22 $\text{kg} \cdot \text{kg}^{-1}$ molding water content clay liner.

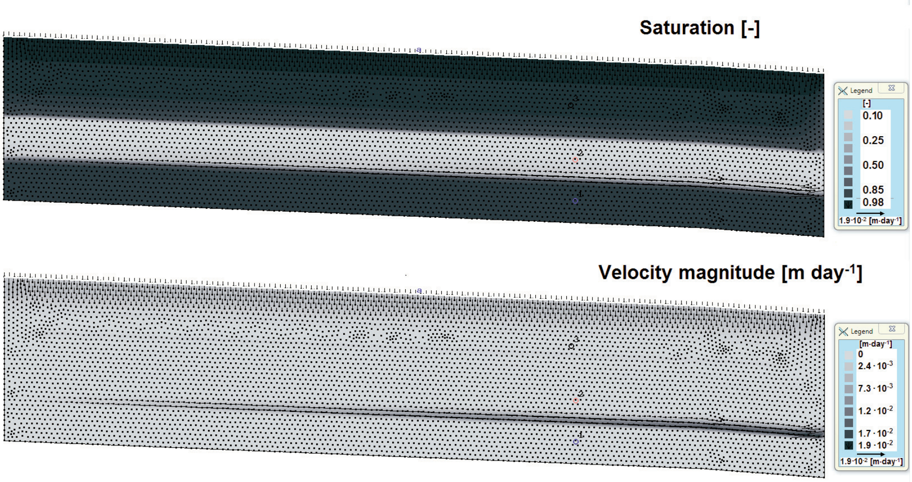

Fig. 6. Contours of saturation degree and velocity magnitude for t = 340 day

It is clearly visible that lateral velocity of flow in drainage layer, directly above the top boundary of compacted clay sealing reaches the highest, dominant values, approx. $2.0 \cdot 10^{-2}$ meters per day, in comparison to water flow in recultivation (range of approx. $2.0 \cdot 10^{-3} – 5.0 \cdot 10^{-3}$m $\cdot$ day^{-1}) and sealing layer (range of $3.0 \cdot 10^{-9}$ m $\cdot$ day^{-1}). As the result, the significant side outflow was observed for the drainage layer. The observed modeled mean daily lateral outflow for the drainage sand layer was approx. $2.0 \cdot 10^{-3}$ m $\cdot$ day^{-1} per m^2, while the modeled mean seepage through the compacted sealing clay liner was in range between $1.5 \cdot 10^{-6}$ and $5.0 \cdot 10^{-9}$ m $\cdot$ day^{-1} per m^2 for molding water content between 0.14 and 0.23 kg $\cdot$ kg^{-1}, respectively. Thus, sealing liners significantly reduces surface water infiltration into waste body. However, the huge lateral outflow through the sand drainage layer limits also increase of sealing layer saturation. The incensement of saturation degree of compacted clay liner in relation to the initial condition was observed only for molding water contents of 0.14 and 0.17 kg $\cdot$ kg^{-1}. So, drying, and shrinkage of clay liner may be possible in case of increased outflow through steep drainage layer.

Conclusions

Our studies are in agreement with literature reports proving a direct relation between molding water content applied during compaction of clay and its saturated water conductivity. We observed a decrease of saturated hydraulic conductivity of compacted clay, from $1.0 \cdot 10^{-10}$ m $\cdot$ s^{-1} to $3.21 \cdot 10^{-11}$ m $\cdot$ s^{-1}, due to increase of applied molding water content from 0.17 kg $\cdot$ kg^{-1} to 0.23 kg $\cdot$ kg^{-1}. Molding water content equal to 0.14 kg $\cdot$ kg^{-1} was insufficient to ensure saturated hydraulic conductivity lower than $1.0 \cdot 10^{-9}$ m $\cdot$ s^{-1}. Additionally, the modeled decrease of seepage percolating through the top liner for the same range of molding water content variability reached two orders of magnitude. However, it must be underlined that according to the significant increase of shrinkage potential for values of molding water content higher than value corresponding to the maximum bulk density obtained, the clay utilized in construction of sealing layer should be compacted on the left, dry side of Proctor's curve, at or below the maximum bulk density. There was also no significant decrease of permeability and seepage volume observed for the right side of Proctor's curve. However, the possibility of soil cracking, reducing the sealing properties of the liner and increasing the possible seepage becomes significant. The above shows that selection of the proper molding water content during construction of the municipal landfill cell liner of the compacted clay material is crucial because it may significantly influence the efficiency of the sealing, preventing migration of the pollutants into the environment. Additionally, the construction of top landfill cover should prevent the increased lateral water flow, which may reduce the possibility of clay sealing layer saturation or resaturation after drying. The high difference of permeability and water storage capacities of drainage and sealing layers required by actual Polish standards may result in inhibited infiltration of water to clay liner.

Acknowledgements

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MODELOWANIE FUNKCJONOWANIA PRZESŁONY SKŁADOWISKA ODPADÓW WYKONANEJ Z ZAGĘSZCZONEGO GRUNTU ILASTEGO

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Abstrakt: Zagęszczone materiały ilaste są powszechnie używane jako materiał uszczelniający zapobiegający migracji zanieczyszczeń antropogenicznych ze składowisk odpadów komunalnych do środowiska naturalnego. Bariery ilaste, zwane także przesłonami, uszczelniają powierzchnię, boki oraz dno składowiska, ograniczając infiltrację wód powierzchniowych oraz przesączenie się odcieków, zazwyczaj dzięki wymaganej przepuszczalności wodnej poniżej $1.0 \cdot 10^{-9}$ m $\cdot$ s^{-1}. Wartość wypadkowa przewodnictwa hydraulicznego zagęszczonej przesłony ilastej oraz jej trwałość uzależnione od procesów skurczu i pęcznienia iłów, są bezpośrednio związane z zastosowaną wilgotnością zagęszczania. Niniejsza praca przedstawia wyniki badań dotyczących wpływu wilgotności zagęszczania gruntu na wartość współczynnika przewodnictwa hydraulicznego w stanie nasyconym, charakterystykę skurczu i pęcznienia oraz właściwości górnej przesłony składowiska odpadów zbudowanej zgodnie z aktualnymi normami z gruntu ilastego. Zaprezentowane badania obejmowały badania terenowe, laboratoryjne oraz studia modelowe. Przepuszczalność badanego gruntu oraz jego właściwości retencyjne zostały przebadane in situ oraz w warunkach laboratoryjnych. Współczynnik przewodnictwa hydraulicznego w stanie nasyconym w warunkach polowych zmierzono za pomocą przepuszczalnomierza polowego BAT GeoNordic, przepuszczalność nasyconą zagęszczonych materiałów ilastych zmierzono w warunkach laboratoryjnych za pomocą przepuszczalnościomierzy do gruntów zagęszczonych H-4145 Humboldt Mfg. Co., zgodnych z ASTM D5856. Charakterystykę retencyjną badanego gruntu po zagęszczeniu w zakresie 0–15 barów wyznaczono za pomocą metody bloku pyłowego oraz komór ciśnieniowych z płytami ceramicznymi. Ocenę właściwości hydraulicznych przesłon wykonanych z badanych materiałów ilastych zrealizowano dla roku hydrologicznego 2012 poprzez modelowanie numeryczne procesu infiltracji przez wybrany fragment przykrycia składowiska odpadów w Rastorf, Niemcy, dostosowany do polskich wymagań prawnych. Badania symulacyjne przeprowadzono za pomocą programu obliczeniowego FEFLOW, DHI-WASY.

Słowa kluczowe: materiały ilaste, przesłony mineralne, przewodnictwo hydrauliczne, modelowanie numeryczne

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AMMONIA AS A SUSTAINABLE FUEL

AMONIAK JAKO ZRÓWNOWAŻONE PALIWO

Abstract: An ammonia evaluation as a potential sustainable fuel in comparison with other fuels was made. Values of laminar burning velocity ammonia at ambient and elevated temperatures 20, 100, 200, 250 °C and pressure 100 and 500 kPa using the data from SAFEKINEX project were estimated.

Keywords: ammonia flammability, burning ammonia-air mixtures, laminar burning velocity

Introduction

With the increasing global population and dwindling energy resources, there is a need to search for alternative energy sources and carriers. They must be able to satisfy the world's growing demand for energy, generating the least possible amount of greenhouse gases and pollutants into the environment. Energy storage in the form of electricity is still a big challenge, on which the researchers from around the world are working. Therefore, only the synthesis of simple chemical compounds, like ammonia and using them as an energy carrier give the possibility of reduction of greenhouse gases emission in the near future [1–4].

Ammonia is a large-scale synthesis product, widely used in many industries [5]. Its global production in 2013 was estimated to approx. 140 million Mg [6]. It is mainly used for agricultural purposes as well as for the production of explosives, synthetic fibers, detergents and pharmaceuticals. The process of its production by Haber-Bosch method, requires a high temperature (~500 °C) and very high pressure (15–30 MPa). The raw material for the process is the most a natural gas [7]. Estimated carbon dioxide emission during ammonia synthesis from natural gas is *ca.* 1.87 Mg of CO_2/Mg NH_3.

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Such a large amount of carbon dioxide emitted, the complexity and technical difficulties of the Haber-Bosch process, are forcing to look for alternative sources of hydrogen, as well as search for new, better ammonia synthesis process [6–8].

Ammonia as an energy carrier

The biggest advantage of ammonia and a high interest of it as a potential fuel are caused by its possible of non CO_2-emission during the synthesis and the combustion process [1, 4]. The combustion is a very complicated process, which progresses with participation of a lot of intermediate products and elementary reactions [9, 10]. The main products of ammonia combustion in the air are: nitrogen, water steam and nitrogen oxides. The amount of nitrogen oxides depend on the kind of mixture and conditions of the process [11]. If the concentration of nitrogen oxides was significant, it might be proposed the selective catalytic reduction as a method to remove them from exhaust gases. The reagent to remove nitrogen oxides might also be ammonia [12].

For the last years hydrogen has been considered as the most promising fuel, but because of its low critical temperature the research about the new and more effective methods of its storage are still in progress [13]. For application a fuel in transportation sector, a very important are: mass and volume of fuel tank, distance range and rate of its fill/regeneration. Low volume energy density of hydrogen creates an advantage of ammonia as a transportation fuel. Compressed ammonia to 1 MPa indicates volume energy density (13.6 GJ m^{-3}) bigger than metal hydrides under pressure 1.4 MPa (3.6 GJ m^{-3}) and also bigger than even actual used fuels, like compressed natural gas to 25 MPa (10.4 GJ m^{-3}). Ammonia can be also the direct source of hydrogen in fuel cells

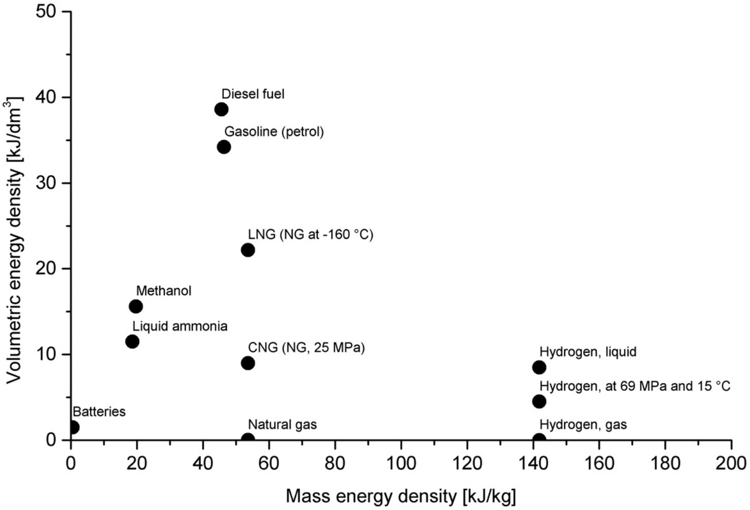

Fig. 1. The comparison of volumetric energy density and gravimetric energy density for different fuels and ammonia [2]

and in the spark-ignition engine [2]. Volume density energy in dependence on mass density energy was shown on the Fig. 1.

Synthesis ammonia by Haber-Bosch method is related inseparably with the hydrogen production process. Currently, the most common methods of hydrogen production are steam reforming of natural gas, partial oxidation of hydrocarbons and coal gasification. It means, that almost entire currently produced hydrogen comes from production process, in which fossil fuels are used. The CO_2-free fuel cannot emit significant amount of greenhouse gases during using of fuel and also during its production. It forces to produce hydrogen and ammonia only with using nuclear or renewable energy [7, 14].

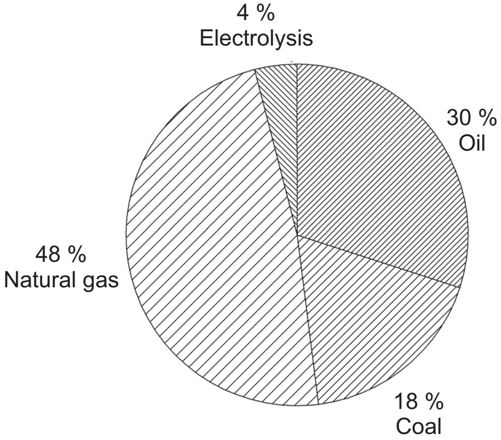

Fig. 2. The participation of different fuels in hydrogen production [7]

In comparison with metal hydrides (H_2 *cont. c.a.* 25 kg/m^3) content of hydrogen in liquid ammonia (condition: 20 ^oC and 0.86 MPa) is above four times bigger (*c.a.* 108 kg/m^3). The consideration of ammonia as a fuel has to include not only its directly combustion in engine, but also possibility of recovery hydrogen from ammonia – at least a part of it in order to increase value of laminar burning velocity [2, 15].

Ammonia cannot be directly used in the spark ignition engine. Despite of its high octane number (110–130), the values of laminar burning velocity of ammonia-air mixtures are too low. The solution of this problem can be an addition of an another fuel with high laminar burning velocity, like *eg* hydrogen. The sufficient amount of hydrogen to increase properties of the combustion can be prepared by thermal or catalytic ammonia decomposition at the expense of some of the energy from its combustion. The cooling effect during the evaporation of ammonia at an appropriate concept of technology can significantly improve the performance of a heat engine [2, 3, 11].

The advantage of ammonia as an energy carrier are also the already existing infrastructure of manufacturing, distribution and more than 100 years of experience in the synthesis, storage and marketing. Ammonia can be stored under similar conditions as propane, *ie* at a pressure of *approx.* 0.8 MPa at ambient temperature. In case of leakage, it is dispersed due to the lower density in comparison to the air [2, 16].

Dangers connected with commercial using of ammonia

Ammonia is a toxic, flammable, colorless gas with a characteristic, suffocating odor. It is easily perceptible in air above 20 ppm concentration. There are known few of severe disasters connected with a production and storage of ammonia [17]. The most significant danger in production and distribution of ammonia is its toxicity and flammability in mixture with the air [16].

In comparison with others fuels, the flammability limits of ammonia under normal conditions are relatively narrow (16–25 % *vol.*), and autoignition temperature is high (651 °C). *Eg.* the flammability limits of others fuels respectively are: hydrogen (4–75 % *vol.*), methane (5–15 % *vol.*), gasoline (1.4–7.6 % *vol.*) and gas oil (0.6–5.5 % *vol.*) [2]. The most significant indexes of explosiveness of gases are: maximal pressure during explosion P_{ex}, maximum rate of pressure rise $(dP/dt)_{ex}$, deflagration index K_G, explosion and detonation limits, minimal ignition energy $E_{\min}$, and autoignition temperature T_s. Maximum rate of pressure rise during explosion and deflagration index are considered as the indices, which the best show dynamic (violence) explosion of gases [18, 19].

In respect to the mathematical notation, the rate of pressure rise $(dP/dt)_{\text{ex}}$ is defined as the maximum value of first derivative with respect to time during the explosion mixture of a precisely determined composition. The rate of pressure rise is dependent from a vessel volume. To describe the explosion phenomena is applied deflagration index K_G, which was presented by expression (1); V is a vessel volume:

$$K_G = \left(\frac{dP}{dt}\right)_{ex} V^{\frac{1}{3}} \tag{1}$$

Laminar burning velocity S_L shows the violence and gas dynamics of the combustion process and it is applied to evaluation of the substance as a potential fuel. During obtaining maximal rate of pressure rise, laminar burning velocity can be approximated by the expression (2); R – vessel diameter, P_{ex} – maximal pressure during explosion, P_i – initial pressure, P – measured pressure, γ – heat capacity ratio (C_P/C_V), dP/dt – current pressure rise. The following expression has been derived for the spherical reactor [20]:

$$S_L \approx \frac{R}{3\,(P_{\text{ex}} - P_i)} \left(\frac{P_i}{P}\right)^{\frac{1}{\gamma}} \left[1 - \left(\frac{P_i}{P}\right)^{\frac{1}{\gamma}} \frac{P_{\text{ex}} - P}{P_{\text{ex}} - P_i}\right]^{-2/3} \frac{dP}{dt} \tag{2}$$

In Tables 1 and 2**,** rates of pressure rise $(dP/dt)_{\text{ex}}$ for ammonia, obtained by Federal Institute for Materials Research and Testing (BAM) were shown. The research were carried out in cylindrical reactor (6 dm^3; initial pressures: 100 and 500 kPa; initial temperatures, T_i: 20, 100, 200 and 250 °C) in within the European project SAFEKINEX [18, 21].

Table 1

The values $(dP/dt)_{ex}$ at initial pressure P_i = 100 kPa [21]

T_i [°C]	$(dP/dt)_{ex}$ [100 kPa/s] (values in brackets show concentration of ammonia in mole percent)								
20	1.87 (15 %)	1.82 (18 %)	3.83 (19 %)	12.29 (21 %)	22.74 (23 %)	30.28 (25 %)	4.37 (30 %)	1.60 (35 %)	
100	3.01 (15 %)	3.2 (17 %)	9.52 (19 %)	35.56 (21 %)	41.26 (23 %)	36.03 (25 %)	8.50 (30 %)	3.15 (35 %)	
200	9.48 (15 %)	16.23 (17 %)	39.62 (19 %)	71.73 (21 %)	71.12 (23 %)	72.45 (25 %)	31.8 (30 %)	11.37 (35 %)	
250	11.71 (15 %)	18.52 (17 %)	41.83 (19 %)	48.35 (21 %)	45.92 (23 %)	42.01 (25 %)	30.67 (30 %)	10.96 (35 %)	3.09 (40 %)

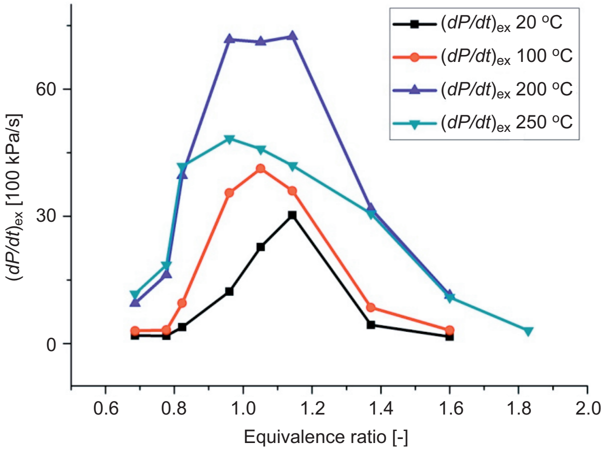

Fig. 3. $(dP/dt)_{ex}$ vs equivalence ratio at in different initial temperature, P_i = 100 kPa [21]

Table 2

The values $(dP/dt)_{ex}$ at initial pressure P_i = 500 kPa [21]

T_i [°C]	$(dP/dt)_{ex}$ [100 kP/s] (values in brackets show concentration of ammonia in mole percent)								
20		63.33 (17 %)	106.32 (19 %)	142.75 (21 %)	204.33 (23 %)	134.02 (25 %)	15.01 (30 %)	5.27 (35 %)	
100	21.6 (15 %)	88.77 (17 %)	118.59 (19 %)	226.86 (21 %)	287.77 (23 %)	237.04 (25 %)	83.91 (30 %)	2.31 (35 %)	
200	71.77 (15 %)	117.79 (17 %)	162.45 (19 %)	186.42 (21 %)	232.54 (23 %)	191.03 (25 %)	114.41 (30 %)	22.09 (35 %)	3.56 (37 %)
250	28.54 (15 %)	56.51 (17 %)	126.62 (19 %)	264.1 (21 %)	301.94 (23 %)	324.31 (25 %)	151.89 (30 %)	63.13 (35 %)	

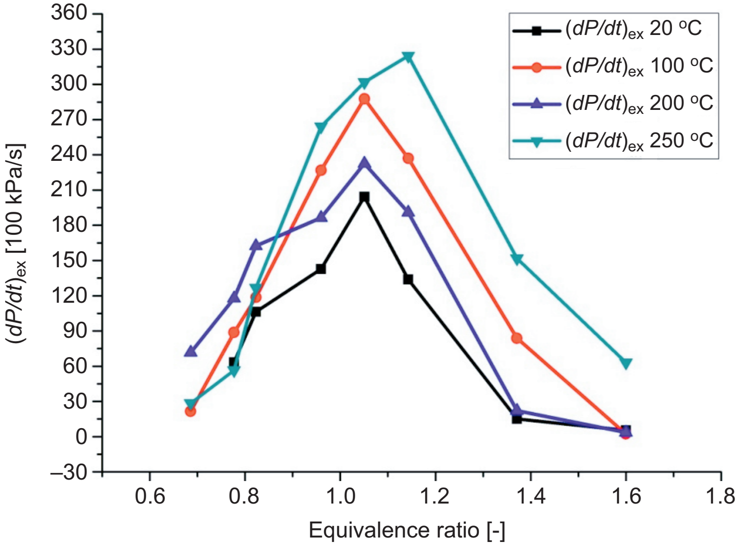

Fig. 4. $(dP/dt)_{ex}$ vs equivalence ratio at in different initial temperature, P_i = 500 kPa [21]

To estimate the value of laminar burning velocity in the point of maximum pressure rise were assumed that the maximum pressure rise was reached while the flame front had not reached the wall of reactor. The data from SAFEKINEX project for ammonia [12] and expression (2) to estimation S_L values were used. The obtained values of laminar burning velocity for initial pressure 100 and 500 kPa respectively in Table 3 and 4 were listed.

Table 3

The estimated values of $S_{L\ ex}$ at initial pressure P_i = 100 kPa

T_i [°C]	$S_{L\ ex}$ [m/s] (values in brackets show concentration of ammonia in mole percent)								
20	— (15 %)	0.116 (18 %)	0.133 (19 %)	0.086 (21 %)	0.051 (23 %)	0.064 (25 %)	0.072 (30 %)	— (35 %)	
100	— (15 %)	— (17 %)	0.053 (19 %)	0.149 (21 %)	0.125 (23 %)	0.127 (25 %)	0.091 (30 %)	— (35 %)	
200	0.107 (15 %)	0.130 (17 %)	0.206 (19 %)	0.301 (21 %)	0.230 (23 %)	0.267 (25 %)	0.160 (30 %)	0.077 (35 %)	
250	0.138 (15 %)	0.161 (17 %)	0.270 (19 %)	0.238 (21 %)	0.202 (23 %)	0.230 (25 %)	0.174 (30 %)	0.089 (35 %)	— (40 %)

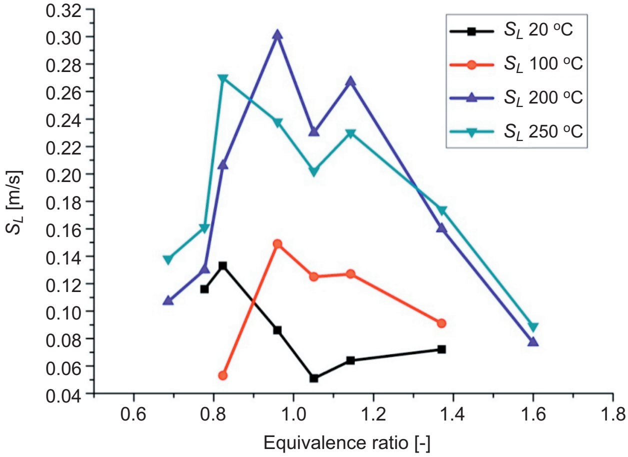

Fig. 5. $S_{L\ ex}$ vs equivalence ratio at different initial temperature, P_i = 100 kPa

Table 4

The estimated values of $S_{L\ ex}$ at initial pressure P_i = 500 kPa

T_i [°C]	$S_{L\ ex}$ [m/s] (values in brackets show concentration of ammonia in mole percent)								
20		0.053 (17 %)	0.052 (19 %)	0.068 (21 %)	0.072 (23 %)	0.060 (25 %)	0.045 (30 %)	— (35 %)	
100	0.066 (15 %)	0.085 (17 %)	0.066 (19 %)	0.123 (21 %)	0.123 (23 %)	0.119 (25 %)	0.064 (30 %)	— (35 %)	
200	— (15 %)	0.113 (17 %)	0.144 (19 %)	0.163 (21 %)	0.197 (23 %)	0.162 (25 %)	0.089 (30 %)	0.048 (35 %)	— (37 %)
250	0.059 (15 %)	0.116 (17 %)	0.199 (19 %)	0.224 (21 %)	0.250 (23 %)	0.291 (25 %)	0.150 (30 %)	0.089 (35%)	

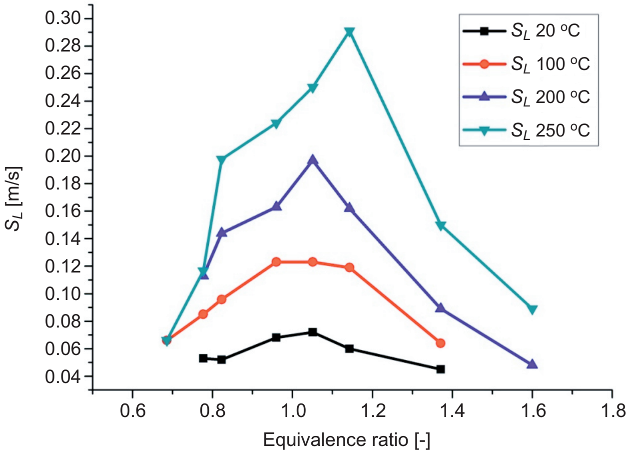

Fig. 6. $S_{L\ ex}$ vs equivalence ratio at different initial temperature, P_i = 500 kPa

Conclusions

Ammonia can be considered as a potential fuel in the short and long term perspective of using it. It has low values of laminar burning velocity but this is not major issue to apply it in spark-ignition engines – *eg* short term solution. Ammonia can also be a hydrogen's precursor in fuel cells – *eg* long term solution. It must be kept in mind that above sample solutions would be reasonable if the energy used to produce ammonia came from renewable sources.

The greatest challenge for ammonia applying in the public space as an energy carrier is its strong toxicity. Simultaneously, there only have been noticed few cases of deadly poisoning, caused by release of ammonia from refrigeration systems into the public space [22].

The explosiveness research of the substances present in public space are always important in aspect of safety. Projects as SAFEKINEX give very important, in aspect of safety data for many substances present in the public space under different conditions.

It is important to underline that the obtained values of laminar burning velocity could contain gross errors, especially under initial conditions 100 kPa and 20 ^{o}C. Despite this, the obtained values are consistent with data in standard conditions in available science literature [23].

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AMONIAK JAKO ZRÓWNOWAŻONE PALIWO

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Abstrakt: W pracy dokonano oceny przydatności amoniaku jako potencjalnego paliwa w odniesieniu do paliw konwencjonalnych. Wykorzystując dane z projektu SAFEKINEX, oszacowano także wartości prędkości spalania laminarnego amoniaku w temperaturze 20, 100, 200, 250 °C przy ciśnieniu 100 i 500 kPa.

Słowa kluczowe: palność amoniaku, spalanie mieszanki amoniak-powietrze, prędkość spalania laminarnego

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THERMAL STABILITY OF POLYPROPYLENE COMPOSITE REINFORCED WITH GLASS FIBRE IN THE OXIDISING ATMOSPHERE

STABILNOŚĆ TERMICZNA KOMPOZYTU POLIPROPYLENOWEGO WZMACNIANEGO WŁÓKNEM SZKLANYM W ATMOSFERZE UTLENIAJĄCEJ

Abstract: Stability of the polypropylene composite with fiber glass (45/55) in the form of low density mat was tested experimentally at increased temperature. It was examined by analyzing the influence of the atmosphere with various oxygen content on the decomposition rate of the polypropylene composite. It has been found that in the air atmosphere, the initial decomposition temperature is close to 200 °C. Lowering the oxygen concentration in the atmosphere to 2 % results in increase of composite decomposition temperature to almost 240 °C. Decomposition components were identified in the methylene chloride extract from composite and in the condensed reaction products. Rate of decomposition conversion at initial stage below 0.2 was estimated as a system of equations: zero order path $r = k_1$ for polypropylene degradation and first order path $r = k_2[O_2]$ for oxidative decomposition. A brief safety analysis is performed identifying the possibility of exceeding an explosion limit under certain conditions. The best way of mitigating the fire/explosion hazard is lowering the oxygen content below 2 % vol., especially for processing of recycled polypropylene.

Keywords: polymer composites, polypropylene composite, thermal stability, thermal decomposition, thermal-oxidising degradation, temperature of degradation

Introduction

Polypropylene is mainly used at the temperature below 100 °C however its processing takes place at increased temperature. In this operation, temperature exceeding 200 °C should be avoided as it triggers a slow process of slow polymer decomposition. It is noted that already at the temperature near 300 °C quite rapid pyrolysis of polymer material occurs and volatile products are created, most of them

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combustible. Oxygen has a large influence on the rate and mechanism of the polymer decomposition. The mixture of evolved flammable components with oxygen may be ignited, releasing energy that drives further pyrolysis, hence fire or explosion hazard appears. Decomposition and ignition of the polymer depends mainly on the form of material, for *eg* porous material are ignited easier and with smaller ignition energy.

The common feature of the majority of organic compounds is their little thermal stability. At increased temperature, they have tendency to decompose and small fragments may easily create gas phase. Additionally, nearly all organic compounds that contain C-H bond are subject to reaction with oxygen: slow – with atmospheric oxygen at ambient temperatures (degradation), faster – in the conditions of increased temperature or/and enhanced oxygen concentration (decomposition). The first stage of this autooxidation process is the formation of hydroperoxides, extremely reactive compounds that may start undesirable behaviour of organic substances, including in-depth decomposition or burning initiation [1, 2]. Similar oxidation paths occur also in the gaseous phase [3]. The complexity of this phenomenon is illustrated by huge spectrum of the oxidation products and spatial heterogeneity of the reaction, already at relatively low temperatures of 80–150 ^{o}C [4–6].

Material's susceptibility to ignition and burning is determined by oxygen index [7]. The higher oxygen index value the less flammable material: below 21 – is flammable, above 28 – non-flammable. Raw polypropylene usually has an oxygen index value varying between 17–29. The polypropylene examined in this study was reinforced by glass fibre filling and, most likely, its index was not modified.

Thermogravimetric analysis of non-stabilised powdered polypropylene heated at different rates in the argon atmosphere points that with increasing of the heating rate, the temperature of the beginning of decomposition shifts towards higher temperature [8]. This shift is caused by the shortening of reaction time at a given temperature and is clearly visible on all publicated thermogravimetric curves. Change of atmosphere from argon to air results in considerably lower degradation temperature, getting close to 235 ^{o}C [8].

A similar value is indicated in the study [9] where, the behaviour of polypropylene and the polypropylene composite with hemp fiber was tested in the air, with the heating rate of 10 K/min. It has been observed that the composite containing 30 % of hemp fiber is more thermally stable than the examined fibres, as well as the pure polypropylene. The temperature at the start of decomposition was nearly the same for all materials tested but the temperature of the highest rate of decomposition was 338 ^{o}C for polypropylene and 360–380 ^{o}C for the composite. Such surprising behaviour is intriguing and requires further understanding in order to specify safe processing conditions for composite materials [9].

An effect of injection temperature (170, 210 and 250 ^{o}C) as well as fibre content (20 and 30 % by mass) in the polypropylene composite with fiber glass was examined [10]. The thermal stability was also tested by heating samples in the nitrogen atmosphere. It has been stated that thermogravimetric curves of pure polypropylene previously processed at various temperatures and curves of the composites, overlapped up to the starting temperature of the decomposition close to 250 ^{o}C. Behaviour of the samples tested at a higher temperature indicated marginal changes of their thermal stability and the composite was slightly more stable as compared with plain polymer.

The main aim of this paper was to propose a reaction model to describe the initial stage of polypropylene composite decomposition, useful to hazard analyses. In order to obtain a set of kinetic parameters for decomposition process, a range of thermogravimetric runs were performed. In addition, some decomposition products has been examined employing GC-MS.

Methodology of measurements

Composite material on the warp of recycled polypropylene (PP) contained ca. 55 % of mass. of glass fiber (GF). The analyzed samples relate to the material in the form of mats, used after the thermal treatment to design and soundproofing car interior. According to the literature information the composite reinforced with glass fiber (30 % of fibre) has similar temperature of melting to the temperature of pure polypropylene [2].

The samples of composite PP/GF (45/55) ca. 50 mg in the form of small chips were heated from the room temperature at the rate of 5 K/min in calorimeter NETZSCH STA 409C. Oxygen-free atmosphere (argon), mixtures of nitrogen with oxygen (with the oxygen content of 21, 11, 8 and 2 % vol.), as well as mixtures of nitrogen with carbon dioxide and oxygen (10 % vol. CO_2 and 2 % vol. O_2) were applied. TG and DTA measurements were conducted with the flow of gas approximately 50 cm^3 per minute

Subject to tests was also residue from the composite degradation collected from the industrial processing oven in which the composite was heated in the air, up to the temperature of 215 ^oC in 35 s of heating cycle, at no air exchange. The condensate has undergone GC-MS analysis and the same analysis was carried out for the methylene chloride extract obtained from the composite. The solvent extraction was made in the Soxhlet apparatus for the composite sample with dimensions 20 × 70 mm with 100 cm^3 of solvent for 24 hrs. Following this, the solvent was evaporated and residue was diluted with methylene chloride to the concentration of ca. 0.1 % of mass. similarly as the condensate sample.

The GC-MS analysis was done on Hewlett-Packard apparatus (gas chromatograph HP 6890 coupled with mass spectrometer MSD 5973) equipped with capillary column HP5MS.

Test results

TG/DTA analysis

During composite heating in the argon atmosphere an endothermic effect of transformation associated with polymer melting was observed at the temperature of 160 ^oC on the DTA curve (Fig. 1), similarly as in raw polypropylene [8]. At higher temperatures distinguished changes suggesting degradation of polymer were observed.

At the temperature of 200 ^oC the composite still did not show the signs of degradation. It is evident that very slow mass sample loss begins to be visible no sooner

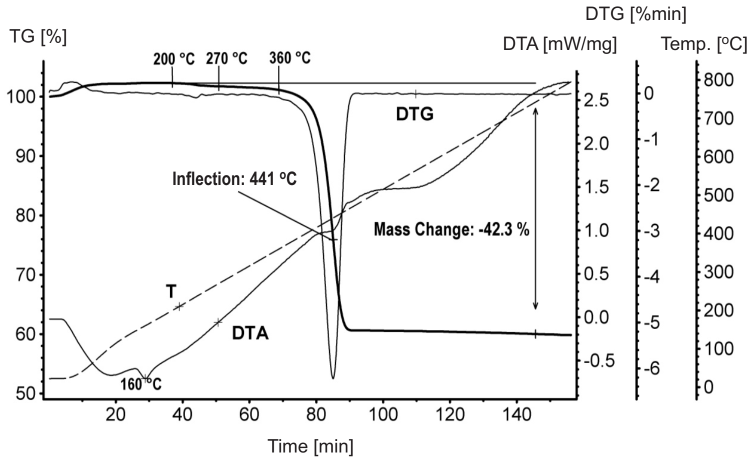

Fig. 1. TG, DTG and DTA curves of PP/GF (45/55) composite under argon atmosphere at 5 K/min

than at the temperature of 260–270 °C. Significant acceleration of mass loss took place at temperature of ca. 360 °C. At the temperature of ca. 440 °C rapid degradation of polymer occured. The total loss of sample mass was ca. 42 % by mass.

The composite behaviour in the presence of oxygen in the gas flowing around the sample was different.

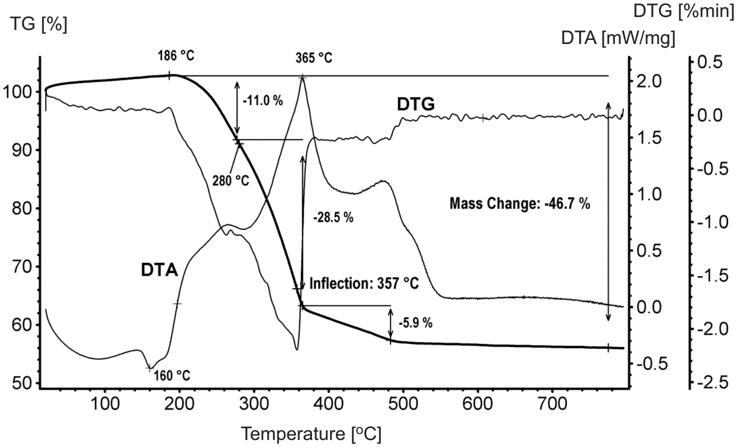

Fig. 2. TG, DTG and DTA curves of PP/GF (45/55) composite under air atmosphere

The following was observed for samples in air (Fig. 2):

– endothermic effect at the temperature of ca. 160 °C associated with the material melting,

– above 186 °C significant acceleration of mass loss occurs; at the temperature of ca. 280 °C it is already close to 11 %,

– maximum rate of decomposition is achieved at the temperature of 357 °C,

– very clear exothermic effect at temperature of ca. 365 °C associated with the material incineration,

– at temperature of ca. 410 °C weight loss is ca. 42 %,

– total weight loss is ca. 46 %, what corresponds to the total content of polymer mass in the composite.

An effect of different content of oxygen in nitrogen was investigated. Figure 3 presents the weight loss of the composite samples.

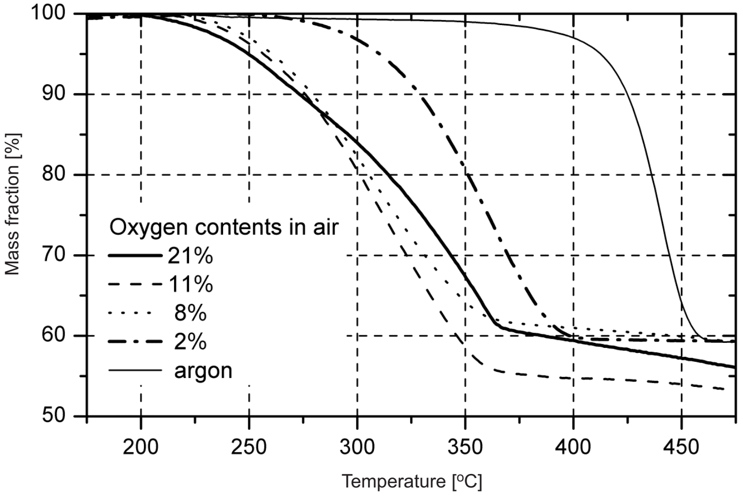

Fig. 3. TG, DTG and DTA curves of PP/GF (45/55) composite under air atmosphere

There is a clear dependence of the content of oxygen on the temperature of initiation of degradation; increase of oxygen content reduces the temperature. Differences in temperature values are small in the atmospheres containing sufficient amount of oxygen (over 10 %). Significant increase in temperature became evident at reduction of the content of oxygen below 2 % of vol. The following temperatures of thermal degradations can be: about 200 °C in the air, 240–250 °C at 2 % of O_2 in N_2 and CO_2, and 260–270 °C in pure argon.

Impact of carbon dioxide on decomposition of polymer is presented in Fig. 4 depicting the of weight loss curve of the composite heated in atmosphere of mixture of nitrogen-carbon dioxide and oxygen.

An attempt has been made to describe the observed changes of the composite mass during heating for small conversion of organic below 0.2. It has been assumed that the purely thermal decomposition can be described with the zero order reaction rate equation $r_1 = k_1$ and influence of oxygen follows first order path $r_2 = k_2[O_2]$. Concentration of oxygen refers to the oxygen concentration in the atmosphere surrounding the composite and $r = r_1 + r_2$ is an overall rate of mass change of

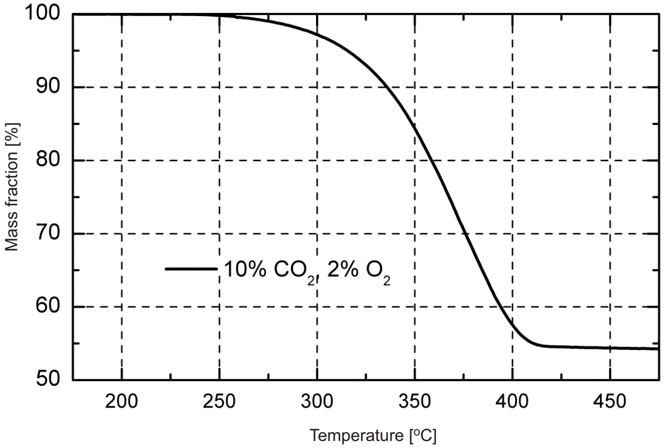

Fig. 4. Thermogravimetric profiles of PP/GF (45/55) in the atmosphere nitrogen – carbon dioxide – oxygen

polypropylene in composite. Coefficients of proportionality k_1 and k_2 have the following dimensions: k_1 [g of polypropylene in composite/s]; k_2 [g of polypropylene in composite/mole fraction of oxygen/s]. It has been assumed that they depend on the temperature and meet the Arrhenius equation: $k = A \exp(-E/(RT))$. Experimental results were used for evaluation of the A and E parameters

$$k_1 = 1.50\ 10^{12} \exp(-204\ 000/(8.314/T)) \quad (1)$$

$$k_2 = 2.74\ 10^{6} \exp(-92\ 000/(8.314/T)) \quad (2)$$

The resulting activation energies are similar to the value obtained for thermal decomposition of polypropylene in the works [5, 8, 11] and is lower than the activation energy given in the work [12]. Figure 5 presents reactivity of the composite considering the derived relations. A simple dependence used reproduces the results of the experiments reasonably well.

Obtained dependence forms the basis for risk analysis during the thermal or thermal-oxidative composite processing. The estimated increase per every hour in the concentration of the reaction products in the oven of volume of 10 m^3, which processes in the air the composite with content of 100 kg/h of pure polypropylene, is close to 0.44 % vol. at a temperature of 200 ^{o}C, assuming the average molecular weight of 60 g/mol. For temperature 220 ^{o}C it is almost 1.13 % vol. and for 240 ^{o}C it comes to 2.72 % vol. Such quantity of volatile substances makes it possible to achieve a lower explosion limit (approx. 2 % vol.), especially when periodic overheating of handled material is possible, *eg* in the emergency state of the device. Therefore, thermal processing of the composite material must take place in an environment of reduced oxygen content or oxygen-free atmosphere.

In order to obtain better understanding of stable decomposition products several analytical methods were applied.

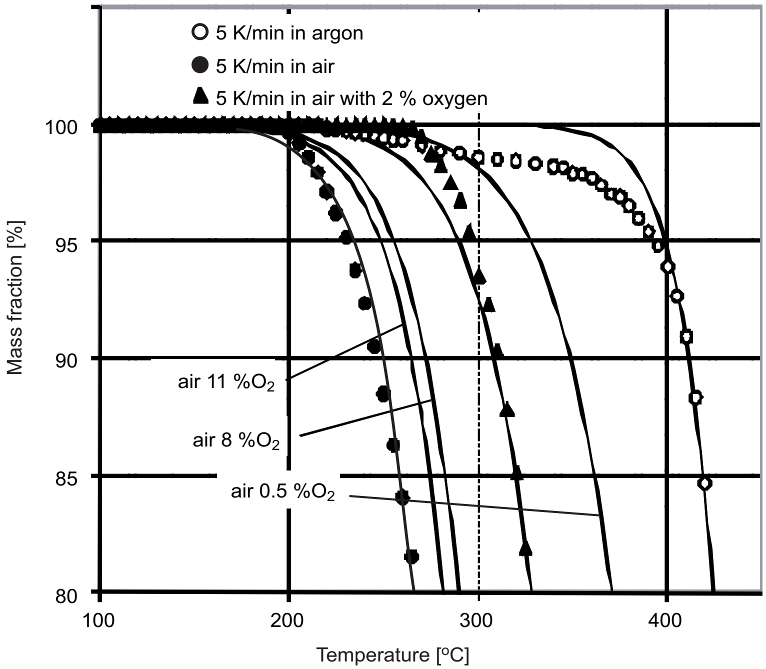

Fig. 5. Calculated and experimental mass change of the polypropylene composite in various atmospheres

GC-MS analysis

In the extract sample, saturated chain hydrocarbons with a wide range of molecular masses were observed. The majority constitute hydrocarbons with the number of carbon atoms from 15 to 24. There are also hydrocarbons C12–C14 as well as hydrocarbons with the number of carbon atoms higher than 25 (Fig. 6).

In the condensate distillation, it was diagnosed that this is a mixture of compounds with high boiling temperature above 325 ^{o}C and the temperature of ignition 228 ^{o}C (open crucible method). This mixture was subjected to analysis to compare with the results obtained during the extract analysis and standard (hexadecane, docosane, octacosane).

The following was established (Fig. 6):

– presence of saturated chain hydrocarbons,

– as opposed to the result with the composite extract, there were not observed hydrocarbons with molecular masses lower than C17 were observed,

– hydrocarbons with boiling temperature above 350 ^{o}C dominated.

The results suggest that the condensate is already free of substances with relatively low boiling point or higher partial vapour pressure. The remaining substances undergo subsequent oxidation yielding small compounds in the gaseous phase.

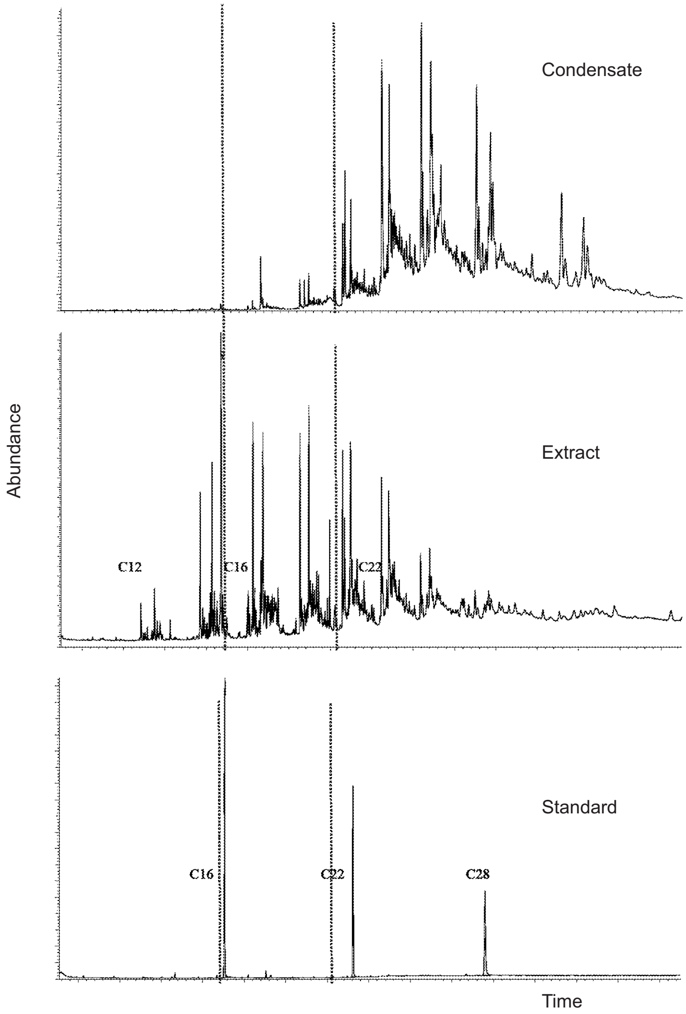

Fig. 6. Chromatograms of the condensate and the composite extract of the polypropylene mat degradation

Summary of results and conclusions

Polyolefines are thermally less stable than their relevant monomers. In the neutral atmosphere, the networking breakdown of the polypropylene commences at the temperature of approximately 160 °C, while decomposition resulting in mass reduction, at the temperature of 260–270 °C. In the examined composite, both C-C bonds and C-H bonds are relatively easily subject to break since every second carbon atom is a quaternary atom. The mechanism of destruction includes cracking of C-C bonds in random places of the chain, leading to disintegration of macromolecules into fragments of different lengths [7]. It is fully confirmed by the results of GC-MS analyse; in the composite extract hydrocarbons from C12 to C26 were found. In the condensate, the mixture of hydrocarbons is already deprived of C12–C22 hydrocarbons.

The oxygen contained in the gas flowing round the composite has an adverse effect on the durability of the examined composite. It enhances destruction of organic substances of the composite, it oxidizes them and at the same time is a key component of the produced post-decomposition flammable mix creating fire/explosive hazard.

Reduction of oxygen concentration in the atmosphere increases the initial degradation temperature. In the air atmosphere this temperature is ca. 200 °C. Reduction in the content of oxygen in the atmosphere to ca. 2 % causes the shift of degradation temperature to ca. 240 °C.

The obtained thermal stability dependencies constitute the basis for safety analysis (thermal stability) of the composite after thermal or thermal-oxidizing treatment in a plant. The data can be further applied for calculation of weight loss for a given industrial process, for the formation of flammable atmospheres in order to define minimum ventilation requirements to avoid accumulation of explosive atmosphere.

A simple correlation was suggested to describe the observed mass changes of the composite during heating in an atmosphere of varying oxygen content. The overall rate of mass change is the sum of polypropylene thermal degradation rate with a constant k_1 and the rate associated with the presence of oxygen (constant k_2). Temperature dependences of both constants were determined. Developed correlations fairly well reproduce the results of the experiments.

Knowledge of the decomposition curves in various atmospheres and at various heating rates enables not only qualitative but also quantitative determination of the safety critical process parameters for the plant, like product throughput, maximal allowed heating rate, residence time, minimal addition of inert gas.

Acknowledgements

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STABILNOŚĆ TERMICZNA POLIPROPYLENU WZMACNIANEGO WŁÓKNEM SZKLANYM W ATMOSFERZE UTLENIAJĄCEJ

Wydział Chemiczny, Politechnika Wrocławska

Abstrakt: Sprawdzano doświadczalnie wrażliwość kompozytu polipropylenu, w postaci maty o niskiej gęstości upakowania, na działanie podwyższonej temperatury. Wrażliwość oceniano, analizując wpływ atmosfery o różnej zawartości tlenu na temperaturę początku rozkładu kompozytu polipropylenu z włóknem szklanym o składzie zbliżonym do 45/55. Stwierdzono, że w atmosferze powietrza, początkowa temperatura rozkładu wynosi ok. 200 °C. Obniżenie stężenia tlenu w atmosferze do ok. 2 % powoduje wzrost temperatury rozkładu kompozytu do ok. 240 °C. Produkty rozkładu zidentyfikowano w kondensacie oraz ekstrakcie kompozytu w chlorku metylenu.

Słowa kluczowe: kompozyt polipropylenowy, stabilność termiczna, rozkład termiczno-oksydacyjny, temperatura rozkładu

Varia

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

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