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

CONTENT OF Ni AND Cr IN WATER AND IN ALGAE FROM SELECTED BLACK SEA BAYS IN THE REGION OF SEVASTOPOL

ZAWARTOŚĆ Ni I Cr W WODZIE I GLONACH Z WYBRANYCH ZATOK MORZA CZARNEGO W REJONIE SEWASTOPOLA

Abstract: Trace metals play an important role in functioning of marine and ocean ecosystems. The particular importance of these elements in ecosystems of salt water basins results from their low concentrations in waters of these basins. The content of trace elements in ocean waters is from a few to several dozen times lower than in fresh waters. Such conditions caused that sea organisms developed, by means of evolution, the ability to intensive absorption of trace elements from water in order to meet the physiological demand for them. However, such abilities can cause excessive bioaccumulation of trace elements in ecosystems with elevated their supply, caused by human pressure or enrichment of the water environment from natural sources. The aim of this paper was to assess the nickel and chromium content in water and in algae from selected Black Sea bays near Sevastopol.

The samples of water and algae were collected in August 2012 from eight bays in the region of Sevastopol (Galubaja, Kozacha, Kamyshova, Kruhla, Striletska, Pishchana, Pivdenna, the Sevastopolska Bay) as well as one sample from the open sea near Fiolent. *Cystoseira barbata* and *Ulva rigida* algae were collected from the same places. The collected water samples were conserved *in situ* and after being brought to the laboratory their contents of nickel and chromium were determined. The collected algae were rinsed in distilled water, dried, and then homogenized and mineralized. Content of the studied elements was determined in mineralisates by AAS method with electrothermal atomization.

It was found that both elements concentrations in water from individual bays were 2–3 times different. The nickel content ranged between 1.74 and 4.14 μgNi $\cdot$ dm^{-3}, and the chromium content was between 1.56 and 5.97 μgCr $\cdot$ dm^{-3}. Water from the Striletska Bay contained the highest amount of the studied elements. The nickel content in the studied algae ranged between 1.967 and 12.87 mg $\cdot$ kg^{-1} d.m., and the chromium content between 0.342 and 7.650 mg $\cdot$ kg^{-1} d.m. A higher accumulation of these elements was found in *Cystoseira barbata* than in *Ulva rigida.* Algae collected in the Sevastopolska Bay contained the highest amount of nickel, and algae from the Pivdenna Bay contained the highest amount of chromium. The content of the studied

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elements in biomass of the algae was not correlated with their concentration in water. On the other hand, a significant correlation between the nickel content in the algae of both species was found. Values of nickel bioaccumulation coefficients in the studied ecosystems were close to values recorded in environments with high human pressure, whereas in the case of chromium they were very low, much lower than values given in available literature. It was a result of a very high concentration of this element in water, and its moderate content in the algae. Generally, a higher content of the studied elements, both in water and in the algae, was found in all the bays than in samples collected in the open sea. The highest threat of the studied metals was found in the Sevastopolska and Pivdenna Bays.

Keywords: Black Sea, pollution, water, algae, nickel, chromium, monitoring, bioaccumulation

Introduction

Trace metals play an important role in functioning of marine and ocean ecosystems. Some of them, for instance iron and manganese, are essential for development of living organisms, whereas physiological role of others has not been discovered yet. According to Aparicio-Gonzalez et al [1] as well as Mehera et al [2], the reason that trace elements are of particular importance to ecosystems of sea and ocean basins is that their concentration in salt waters is very low. Concentration of these elements in ocean waters is from a few to several dozen times lower than in fresh waters. Moreover, bioassimilability of trace elements in the sea environment is usually lower than in freshwater ecosystems. Such conditions caused that sea organisms developed, by means of evolution, the ability to intensively absorb trace elements from water in order to meet the physiological demand for them. However, such abilities can cause excessive bioaccumulation of trace elements in organisms living in ecosystems with elevated supply of these elements, caused by human pressure or enrichment of the water environment from natural sources [3]. Such conditions usually occur in coastal zones or estuaries, with low depth, where good thermal conditions and a higher amount of biogenic substance can be found. In coastal zones, shallow bays and estuaries, there are good conditions for development of phytoplankton, macroalgae as well as a lot of animal species.

Chromium is an element widely used in many fields of human activity, that is why its elevated contents in sewage, both industrial and municipal, are often found. Chromium is widely used in the tannery industry, in protective coatings for metal objects, in paints, and in biocidal agents [4, 5]. This element enters the water environment in consequence of leaching processes from protected surfaces, or along with industrial and municipal sewage. This element is delivered to seas and oceans with river waters, and together with dry and wet deposition. River supply has limited importance for ocean waters, since a greater part of chromium load remains in estuary areas or in coastal regions [6].

Nickel is an element commonly occurring in the water environment. In zones of strong human impact on the environment, elevated concentration of this element is always found, because it is widely used in many fields of human activities. It gets into the water environment from sewage, both industrial and municipal, and as a result of dry and wet deposition. Nickel gets into seas and oceans from materials transported by rivers and as a result of atmospheric deposition. In ocean ecosystems, atmospheric deposition of this element plays the greatest role. Delivery of nickel together with river waters may be of high importance in coastal areas, in estuaries, and inland seas.

Nickel in river water, as a result of changes in salinity arising out of mixing river waters with sea waters, quickly migrates to bottom sediments, which leads to its increased concentration on small areas. In such regions, high bioaccumulation of this element in organisms from all levels of the food chain is often observed [7, 8]. The reaction of most sea waters favors the occurrence of nickel mainly in the form of Ni^{2+}. Increase in pH values favors the formation of hydroxides of this element. Under conditions of high redox potential, this metal is generally adsorbed on iron and manganese compounds, whereas under anaerobic conditions it forms insoluble nickel sulfide. It is an element indispensable for life of plants and land animals. Its physiological role in aquatic animals has not been discovered yet. Symptoms of toxicity of excessive amount of nickel in marine ecosystems are rare to be seen, but the danger from this element is connected with its genotoxic effect [9].

The aim of the research was to assess the content of nickel and chromium in water and in algae from selected Black Sea bays in the region of Sevastopol.

Material and methods

To reach the established goal, samples of water from 8 bays in the region of Sevastopol as well as one sample from the open sea were collected in August 2012. The samples were collected from the top layer of water (from the depth of 0–120 cm) using a scoop sampler with 200 cm^3 capacity. The cumulative sample, with a volume of 3 dm^3, consisted of 15 initial samples with a volume of about 200 cm^3, collected in different points which had been averaged. An average laboratory sample had volume of 500 cm^3. Sample collection points were selected so as a sample as representative as possible for a whole bay. In order to do so, data on water movements and on flow of sea currents were used. The samples were collected from the following bays: Galubaja, Kozacha, Kamyshova, Striletska, Kruhla, Pishchana, Pivdenna, and the Sevastopolska Bay, as well as from the open sea in the region of Fiolent (Fig. 1).

Samples of *Cystoseira barbata* and *Ulva rigida* algae were collected in the same points. The cumulative sample of the algae was a sum of approximately 10 initial samples with the mass of approximately 50 g f.m. each. The laboratory sample was identical with the cumulative sample and amounted approximately 200 g. The selected species of algae are common in the studied area. Due to high capacity for accumulation of heavy metals, they are often used in the evaluation of marine ecosystems pollution with trace elements. Water samples were conserved *in situ* with concentrated nitric acid (of 65 %), in a quantity of 2 cm^3 per each 100 cm^3, and next being brought to the laboratory. Whereas the algae were washed in distilled water, dried at a temperature of 65 ^oC, and homogenized. Laboratory samples of the algae were subjected to wet mineralization in a closed system with the use of microwave energy. The analytical sample amounted to approximately 0.5 g. The material was digested in a mixture of HNO_3 and H_2O_2 (in the 5:1, *v*/*v* ratio). Water samples to be analyzed were thickened ten times. Concentration of nickel and chromium in the obtained solutions was determined

Fig. 1. Points of sampling

by atomic absorption spectrometry with electrothermal atomization, in an M6 device manufactured by Thermo. Nickel was determined at a wavelength of 232.0 nm. The limit of determination for nickel in the applied methods of measurement amounted to 12 $\mu g \cdot kg^{-1}$ d.m. of the biological material, and 0.5 $\mu g \cdot dm^{-3}$ water, and the uncertainty of measurement was ±7 %. Chromium was determined at a wavelength of 357.7 nm. The limit of determination for this element in the applied methods of measurement amounted to 2.5 $\mu g \cdot kg^{-1}$ d.m. of the biological material, and 0.09 $\mu g \cdot dm^{-3}$ water, and the uncertainty of measurement was ±7 %. Certified reference material CRM 16–050 was used to check the correctness of the analyses.

Results and discussion

The nickel concentration in the water collected from individual research points in the region of Sevastopol was within the range from 1.74 to 4.14 $\mu gNi \cdot dm^{-3}$ (Fig. 2).

The mean content of this element was 2.47 $\mu g \cdot dm^{-3}$, and the relative standard deviation (RSD) was 35 %. The lowest nickel concentration was recorded in the water collected in the open sea. Concentrations of this element in the water collected from the Galubaja, Kruhla, Pishchana, and Pivdenna Bays were little different (between 1 and 10 %) than the contents found in a sample from the open sea. It suggests that in those bays there are no significant sources of pollution with this element, and there is no risk of its accumulation in individual parts of biocoenosis. Water from the other bays showed an enrichment in nickel. The highest nickel concentration was determined in the water from the Striletska Bay, and then from the Kozacha, Sevastopolska and

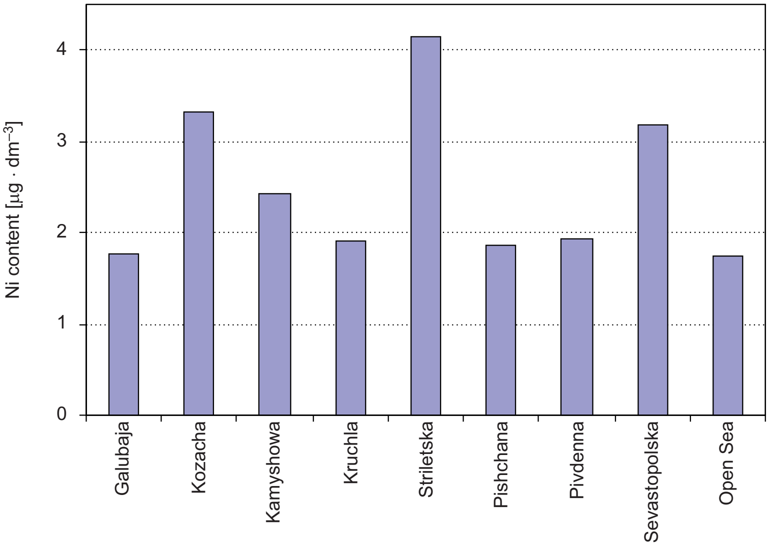

Fig. 2. Content of nickel in water

Kamyshova Bays, in which 2.4, 1.9, 1.8 and 1.4 times more nickel was found, respectively, than in the open sea water.

Sea algae have high affinity to trace elements. Due to the specificity of physiological processes, they can accumulate extremely high amounts of trace elements, even in environments with low content of them in the abiotic parts of the ecosystem, particularly in water [10]. Thanks to this, they can be used as sorbents of trace elements or for bioindication of marine ecosystems pollution [11, 12] as well as freshwater ecosystems [13] with these elements.

The *Cystoseira barbata* algae contained between 1.16 and 3.29 times more nickel than *Ulva rigida*. The nickel content in the *Cystoseira barbata* algae varied from 3.833 to 12.87 mg · kg^{-1} d.m. (Fig. 3), and the relative standard deviation was 37 %. The lowest amount of nickel was found in algae of the species from the Galubaja Bay, by 24 % lower than in the algae collected on the open sea. The content of this element in *Cystoseira barbata* from most of the other bays was between 36 and 50 % higher than in the algae collected in the open sea, which contained 5.075 mgNi · kg^{-1} d.m. Only algae from the Sevastopolska Bay contained approximately 2.5 times more of this metal. Many authors draw attention to considerable differences in the nickel content in algae collected at points located close to one another, with various intensity of human pressure or other water parameters, shaping the bioavailability of this element [14, 15].

The highest amount of nickel (8.867 mgNi · kg^{-1} d.m.) was found in *Ulva rigida* from the Sevastopolska Bay, and its lowest amount (1.967 mgNi · kg^{-1} d.m.) in the algae collected in the Striletska Bay (Fig. 3). The nickel content in samples from most of the bays (Kruhla, Kamyshova, Kozacha, Galubaja, and Striletska) was lower (between 3 and 42 %) than its content determined in the algae from the open sea, which

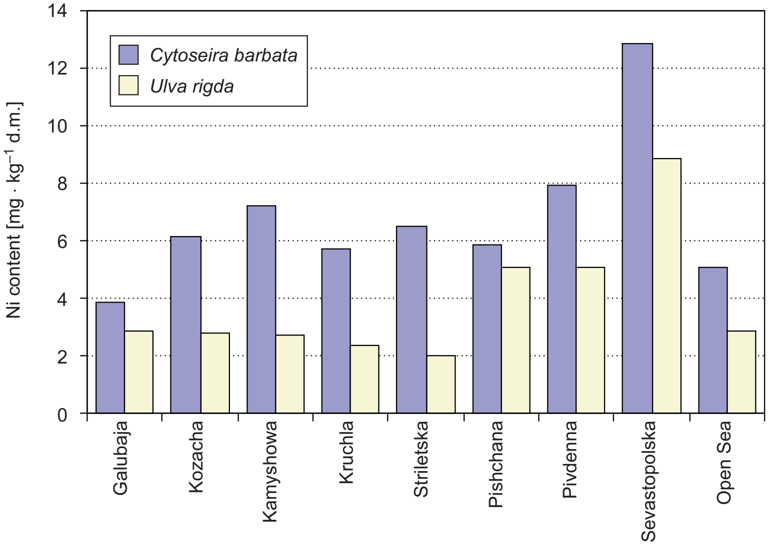

Fig. 3. Content of nickel in macroalgae

contained 2.892 mgNi · kg^{-1}. Nickel contents determined in *Ulva rigida* from the Pivdenna, Pishchana, and especially Sevastopolska Bays were 1.75, 1.76 and 3.07 times higher, respectively, than in the algae collected in the open sea, which points out to a danger of excessive accumulation of this metal in organisms occurring in these ecosystems.

The statistical analysis showed that the nickel content in the biomass of the algae did not correlate with its concentration in the water. On the other hand, a significant correlation between the nickel content in both algae was found ($r_{0.05} = 0.843$).

In most cases, nickel contents in algae determined in the authors' own research are low and close to the content of this element in algae from areas with low human pressure index. Brito et al [16] provide nickel contents several times higher in algae of different species from a region with high level of human pressure in Brazil. The nickel content in the algae from *Ulva* genus collected in the San Jorge Bay in Argentina varied from 0.9 to approximately 4 [17], and was close to results obtained in the authors' own research. Caliceti et al [18] provide 2.6 mgNi · kg^{-1} d.m. as the mean nickel amount in *Ulva rigida* from the Venice Lagoon, and 1.8 mgNi · kg^{-1} d.m. in *Cystoseira barbata* at insignificant differences in content of this element in the algae collected in regions with a various level of human pressure. Wallenstein et al [19] provide a much lower nickel content, approximately 1 mgNi · kg^{-1} d.m., in *Cystoseira humilis* from areas near the Azores from stands with different intensity of anthropopressure. The nickel content in green algae collected in the coastal zone of the Arabian Gulf in the polluted region of Saudi Arabia varied between 25 and 44 mgNi · kg^{-1} [20]. On the other hand, Rodríguez-Figueroa et al [21] provide 28 mgNi · kg^{-1} d.m. as the maximum nickel content in algae from the Mexican Gulf in the region of impact of a copper mine.

Dhaneesh et al [22] provide very low contents of this element, below 0.2 mgNi · kg^{-1} d.m., in algae from the Indian Ocean from areas near the Maldives. The nickel content in the algae for consumption in Spain varied in the wide limits, between 1.2 and 73 mgNi · kg^{-1} d.m., and in the case of *Ulva rigida* between 5.61 and 6.14 mgNi · kg^{-1} d.m. [14]. The nickel content in algae collected from a few estuaries of Western Australia was between 1 to approximately 10 mgNi · kg^{-1} d.m. [23]. At the same time, algae collected in Admiralty Bay in Antarctica, which is an area of insignificant anthropopressure, contained less than 1 mgNi · kg^{-1} d.m. [24].

The values of the bioaccumulation coefficient for nickel in the algae utilized in biomonitoring ranged widely from 475 to 2797 for *Ulva rigida,* and from 1562 to 4111 for *Cystoseira barbata* (Table 1).

Table 1

Values of bioaccumulation coefficients (BC) of nickel and chromium in algae from individual studied points

Number	Sampling points	Bioaccumulation coefficent of Ni		Bioaccumulation coefficent of Cr	
		Cystoseira barbata	*Ulva rigida*	*Cystoseira barbata*	*Ulva rigida*
1	Galubaja Bay	2178	1595	156	124
2	Kozacha Bay	1860	836	371	164
3	Kamyshowa Bay	2975	1112	418	371
4	Kruhla Bay	2980	1226	283	243
5	Striletska Bay	1562	475	156	127
6	Pishchana Bay	3168	2737	644	960
7	Pivdenna Bay	4111	2621	3493	1077
8	Sevastopolska Bay	4059	2797	2016	237
9	Open Sea	2917	1662	288	219

The highest value of this coefficient for algae of both species was found in the Sevastopolska Bay, 4059 and 2797 for *Cystoseira barbata* and *Ulva rigida,* respectively. The lowest values of the bioaccumulation coefficient for nickel were found in the algae from the Striletska Bay. Low values of this parameter at that research point are the result of a high nickel concentration in water, which was not reflected in greater uptake of this metal by the studied organisms. Melville and Pulkownik [23] provide values of the bioaccumulation coefficient for nickel in different species of algae gathered from several estuaries of Western Australia similar to the ones determined in the authors' own research.

A statistical analysis did not show a significant correlation between nickel content in the water and algae. The highest concentration of this metal was recorded in the water from the Striletska and Kozacha Bays, and in the algae collected from the Sevastopolska, Pivdenna and Kamyshchowa Bays. Therefore, concentration of elements in water is not a reliable index of environmental risk, which is pointed out by a number of researchers [11, 12, 16, 25]. Only determination of accumulation of elements in living organisms may provide reliable information on environmental pollution. However, it is important to choose adequate animal or plant species, because the assimilability of trace elements does not depend only on environmental factors, but the intensity of uptake of trace elements is influenced also by population, species, and even ontogenetic predispositions [12, 16, 25]. Improper selection of organisms for bioindication may lead to obtainment of distorted results.

Chromium concentration in the water samples collected from individual research points ranged from 1.56 to 5.97 μgCr · dm^{-3} (Fig. 4), and the mean for all the samples was 3.154 μg Cr · dm^{-3}.

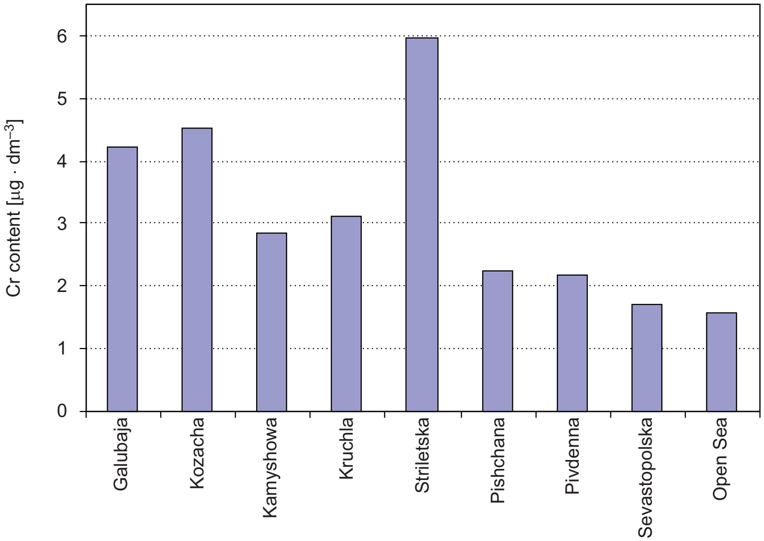

Fig. 4. Content of chromium in water

A high diversity in the content of this element in water from individual research stands was found. The relative standard deviation for chromium water concentration was 46 %.

Chromium is a special element in the sea environment. It can occur at different degrees of oxidation, but only compounds that contain Cr(VI) and Cr(III) forms are stable enough to occur in natural environment. Its toxicological effects in biocoenoses depend on the degree of oxidation. In waters with high redox potential, the dominant form is Cr(VI), which may constitute even more than 90 % of the total amount of this element [26]. Chromium in the form of Cr(VI) compounds is well soluble in water, whereas chromium in the reduced form is slightly soluble, and under conditions of oxygen deficit its quick binding with bottom sediments can be observed. Moreover, the oxidized form of chromium is significantly more easily uptaken by living organisms, which intensifies the problem of water ecosystems being polluted with this element. Chromium in the Cr(III) form is indispensable for proper functioning of mammals. It participates in the metabolism of sugars and lipids, as well as regulation of blood sugar level [27]. Concentration of this element in sea and ocean waters is generally below 1 $\mu g \cdot dm^{-3}$ [28], and the natural content of this element in water is below 0.2 $\mu g\ Cr \cdot dm^{-3}$ [29]. However, nickel concentration in fresh waters is approximately 10 times higher.

The least chromium was recorded in the water collected in the open sea. Chromium concentration in the water collected from all the bays suggests enrichment in this element. The water taken in the Striletska Bay, and then in the Kozacha and Galubaja Bays contained the most chromium, *ie* 3.75, 2.88 and 2.66 times more, respectively, than the water collected in the open sea. Chromium concentrations in water, determined in the authors' own research, are high and characteristic for ecosystems polluted with this element. Such chromium contents in water can endanger organisms living in these ecosystems, as well as people who eat seafood obtained in these regions. Chromium content in waters of Sargasso Sea was significantly lower and varied between 0.13 and 0.3 $\mu gCr \cdot dm^{-3}$ [26].

The *Cystoseira barbata* and *Ulva rigida* algae contained various amounts of chromium, between 0.342 and 7.650 $mgCr \cdot kg^{-1}$ d.m. (Fig. 5), 1.525 $mgCr \cdot kg^{-1}$ d.m. on average. Mean chromium contents in the algae of these species were 2.039 and 1.011 $mgCr \cdot kg^{-1}$ d.m., respectively. The *Cystoseira barbata* algae collected in the Pivdenna Bay contained the highest amount of this element, and the ones collected in the Sevastopolska Bay contained approximately 2 times less. Whereas in the case of the *Ulva rigida* algae, the highest amount of chromium was found in samples collected in the Pivdenna and Pishchana Bays. The *Cystoseira barbata* algae collected at research points contained between 1.09 and 8.75 times more chromium than *Ulva rigida*. Only in the Pishchana Bay a reverse relation was recorded, and the *Ulva rigida* algae contained 1.57 times more chromium than *Cystoseira barbata*. Chromium content in algae from

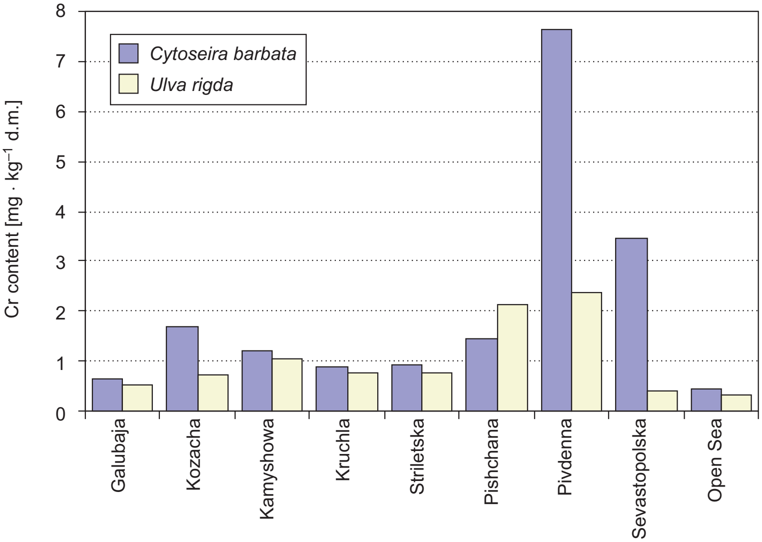

Fig. 5. Content of chromium in macroalgae

unpolluted areas fluctuates between 1 and 3 mgCr · kg^{-1} d.m. [15]. The statistical analysis did not show a significant correlation between the content of this element in water and biomass of the studied algae. Other authors [25, 30] have also determined that concentration of this element in water is rarely significantly correlated with its content in living organisms.

A significantly higher variability in the chromium content in the algae collected from individual research points, compared with the variability in concentration of this element in the water, was found. The highest chromium content in both species of algae was found in the algae living in the Pivdenna Bay, and in that bay also the area with the highest risk to living organisms was defined. Chromium contents in different species of algae taken from the Aegean Sea in coastal regions of Turkey were slightly higher than the ones obtained in the authors' own research, and concentration of this element in water was at a several times lower level than its concentrations present in the water of the bays of the Sevastopol region [30]. Like in the authors' own research, these authors found a higher accumulation of this element in the algae from the *Cystoseira* genus compared with the content of this element in the algae from the *Ulva* genus.

Brito et al [16] provide approximately twice higher contents of this element in biomass of different species of algae from areas with high anthropopressure index in Brazil, whereas accumulation of this element in the algae collected in the Turkish coastal zone of the Black Sea was comparable to the one obtained in the authors' own research [31]. These authors found a significant relationship between the level of human pressure and the chromium content in algae. In areas with the highest level of anthropopressure [31], chromium accumulation was comparable to the one determined in the authors' own research in the Pivdenna Bay. Caliceti et al [18] provide approximately 1 mgCr · kg^{-1} d.m. as the mean chromium content in the *Cystoseira barbata* algae collected from the Venice Lagoon in regions with different intensity of anthropopressure. The contents of this element in the algae from the *Ulva* genus were higher, approximately by a half, than their accumulation in *Cystoseira*. In the authors' own research, the chromium contents in the algae were generally similar to the ones found in the algae collected in the Tanapag Lagoon in a region of the Marian Islands [15]. Samples collected from the Sevastopol and Pivdenna bays were exceptions. In these samples, contents of this element were significantly higher than the ones found by those authors. Chromium contents in *Ulva rigida* and *Cystoseira barbata* collected in the Bulgarian coastal zone of the Black Sea [32] were similar to the ones found in this research in points with the lowest accumulation of this element. In the authors' own research, chromium contents were higher than the ones presented by these authors only in the algae collected in the Sevastopolska and Pivdenna Bays.

Values of bioaccumulation coefficient for chromium in the studied algae range widely, from 124 to 3493 (Table 1). The highest values of bioaccumulation coefficients in both algae species were observed in the Pivdenna Bay: 3493 for *Cystoseira barbata* and 1077 for *Ulva rigida*. The lowest value of the bioaccumulation factor for chromium in the studied organisms was observed in the Galubaja Bay, 156 for *Cystoseira barbata* and 124 for *Ulva rigida* (Table 1). Literature data indicate much higher bioaccumulation factors for chromium in macroalgae from various regions of the world. Akcali and

Kucuksezgin [30] provide values of this factor in algae collected from the Aegean Sea reaching from a few to a dozen or so thousand. Melville and Pulkownik [23] state that the values of the bioaccumulation coefficient for chromium in different species of algae collected from several estuaries of Western Australia are from a few to several dozen thousand.

Conclusions

1. Chromium and nickel concentrations in the water collected from individual bays and from the open sea in the region of Sevastopol suggest anthropogenic enrichment. Such contents, according to literature data, suggest that there is a risk of excessive bioaccumulation of these elements.
2. Nickel contents in the studied algae were not high, but the differences in accumulation of this element in the organisms collected in individual bays point out to a potential risk to living organisms.
3. Chromium contents in the studied algae were low and only accumulation of this element in the samples collected in the Pivdenna Bay was at a level found in polluted environments.
4. Bioaccumulation coefficients for nickel in the studied ecosystems were close to its values in environments with high anthropopressure index, provided in scientific literature.
5. Bioaccumulation coefficients for chromium in the studied algae were very low, much lower than their values provided in literature. It was a result of a very high concentration of this element in water at its moderate content in the algae.
6. Generally, a higher content of the studied elements (both in water and in the algae) was found in all the bays compared with the samples collected in the open sea. The highest threat of the studied metals was found in the Sevastopolska and Pivdenna Bays.

Acknowledgements

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ZAWARTOŚĆ Ni I Cr W WODZIE I GLONACH Z WYBRANYCH ZATOK MORZA CZARNEGO W REJONIE SEWASTOPOLA

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Abstrakt: Metale śladowe odgrywają ważną rolę w funkcjonowaniu ekosystemów morskich i oceanicznych. Szczególne znaczenie tych pierwiastków w ekosystemach zbiorników wód słonych wynika z bardzo małych ich stężeń spotykanym w wodach tych akwenów. Zawartość pierwiastków śladowych w wodach oceanicznych jest od kilku do kilkudziesięciu razy mniejsza niż w wodach słodkich. Takie warunki sprawiły, że organizmy morskie wykształciły na drodze ewolucji zdolność do intensywnego pobierania pierwiastków śladowych z wody w celu zaspokojenia zapotrzebowania fizjologicznego na nie. Takie zdolności mogą jednak powodować nadmierną bioakumulację pierwiastków śladowych w ekosystemach o podwyższonej ich podaży, spowodowanej antropopresją lub wzbogaceniem środowiska wodnego ze źródeł naturalnych. Celem pracy była ocena zawartości niklu i chromu w wodzie oraz glonach z wybranych zatok Morza Czarnego w okolicach Sewastopola.

Próbki wody oraz glonów pobrano w sierpniu 2012 r. z ośmiu zatok w rejonie Sewastopola (Gałubaja, Kozacha, Kamyshova, Kruhla, Striletska, Pishchana, Pivdenna, Sewastopolska) oraz jedną próbkę z otwartego morza w okolicach Fioletu. Z tych samych miejsc pobrano glony *Cystoseira barbata* i *Ulva rigida.* Pobraną wodę konserwowano na miejscu i po przywiezieniu do laboratorium oznaczono w niej zawartość niklu i chromu. Pobrane glony wypłukano w wodzie destylowanej, suszono, a następnie homogenizowano i mineralizowano. W roztworach oznaczono zawartość badanych pierwiastków metodą ASA z atomizacją elektrotermiczną.

Stwierdzono 2–3-krotne różnice stężenia obydwu pierwiastków w wodzie z poszczególnych zatok. Zawartość niklu mieściła się w zakresie od 1,74 do 4,14 μgNi $\cdot$ dm^{-3}, a chromu w zakresie od 1,56 do 5,97 μgCr $\cdot$ dm^{-3}. Najwięcej badanych pierwiastków zawierała woda z zatoki Striletska. Zawartość niklu w badanych glonach wahała się w zakresie od 1,967 do 12,87 mg $\cdot$ kg^{-1} s.m., a chromu od 0,342 do 7,650 mg $\cdot$ kg^{-1} s.m. Stwierdzono większe nagromadzenie tych pierwiastków w *Systoseira barbata* niż w *Ulva rigida*. Najwięcej niklu zawierały glony pobrane w zatoce Sewastopolskiej, a najwięcej chromu zawierały glony z zatoki Pivdenna. Zawartość badanych pierwiastków w biomasie glonów nie była skorelowana z ich stężeniem w wodzie. Stwierdzono natomiast istotną korelację między zawartością niklu w glonach obydwu gatunków. Wartości współczynników bioakumulacji niklu w badanych ekosystemach były zbliżone do notowanych w środowiskach o dużym nasileniu antropopresji, natomiast w przypadku chromu były bardzo małe, dużo mniejsze niż podawane w dostępnej literaturze. Powodem było bardzo duże stężenie tego pierwiastka w wodzie i umiarkowanej jego zawartości w glonach. Generalnie we wszystkich zatokach stwierdzono większą zawartość badanych pierwiastków (zarówno w wodzie, jak i w glonach) niż w próbkach pobranych na otwartym morzu. Największe zagrożenie badanymi metalami stwierdzono w zatokach Sewastopolska i Pivdenna.

Słowa kluczowe: Morze Czarne, zanieczyszczenia, woda, glony, nikiel, chrom, monitoring, bioakumulacja

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ASSESSMENT OF AIR CONTAMINATION WITH SELECTED RADIOISOTOPES NEARBY CEMENT PLANT USING MOSS BAG METHOD

OCENA STANU ZANIECZYSZCZENIA POWIETRZA WYBRANYMI RADIOIZOTOPAMI W POBLIŻU CEMENTOWNI Z UŻYCIEM METODY WORECZKOWEJ

Abstract: Mining and processing industry represents a potential source of radioisotopes contaminating the nearest environment. In order to estimate conditions of the environment in the vicinity of cement plant moss bag biomonitoring method was used. The aim of the study was to assess the relationship between the extent of air pollution with ^{40}K, ^{137}Cs, ^{210}Pb and the distance from the cement plant. The share of various radiation sources in the total ^{210}Pb activity concentration in mosses after exposure was also analyzed. Sampling sites were located in the forest near Opole (PL), in a line and at different distances from the cement plant. In test two types of moss bags, exposed simultaneously in the same places, were used. In the studies, activity concentrations of gamma-radioactive isotopes were determined in samples of moss before and after the exposure. In investigations the gamma-spectrometer with a germanium detector was used. From the obtained results the Relative Accumulation Factors (*RAF*) were calculated. In order to assess the extent to which radionuclides activity depends on the distance from the cement plant, correlation coefficients were calculated. It is hard to estimate the trends of radionuclides activity concentration changes with distance from the cement plant due to substantial discrepancies in the results. No significant relationship of radionuclides deposition on the distance from the cement plant was noticed.

Keywords: Relative Accumulation Factor (*RAF*), radioisotopes, moss bag method, cement plant

Introduction

For many years mining and processing industry significantly burden the environment. In the case of the Opole region (southern Poland) it is associated mainly with limestone mines and cement plants. They represent a potential source of radioisotopes that can spread over various distances. Cement plants use as feedstock limestone, marly

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limestone, marl and clay containing natural radionuclides that are released into the air under high temperature applied during the cement production process. The volatile isotopes ^{222}Rn, ^{210}Po and ^{210}Pb are emitted in the gaseous form or as a precipitate and particulate matter, increasing radioactivity around these industrial plants [1–3].

To assess the air contamination from anthropogenic sources in the vicinity of industrial and urban areas the moss bag biomonitoring technique is frequently used. These method was introduced by Goodman and Roberts in the 80. of 20th century. Since then the moss bag method was repeatedly utilized to assess radioactive contamination near nuclear power plants, after nuclear weapon tests and after nuclear plants accidents [4–8].

The common application of mosses is mainly caused by their relative high efficiency in heavy metals and radioisotopes accumulation. Mosses do not have the epidermis and cuticle, which greatly facilitates the entry of contaminants into the cells. They have no roots, so they collect nutrients only from precipitation and dry deposition. It is assumed that concentration of chemical compounds in the mosses biomass corresponds to deposition from the air [9–11].

Mosses were used, among others, in assessment of radioactive pollution in the southern Poland areas [12–13]. Mosses *Ctenidium molluscum* were also used as radiodeposition bioindicators in north-east Italy [14]. In 1985–2004, in the Ural Mountains, radiodeposition of caesium was determined in the mosses *Hylocomium*, *Pleuroziumand Plerozium* [15]. Radiocaesium activity in the mosses *Pleurozium schreberi* and *Dicranum polysetum* was also studied by Horrill [16]. Both mosses and lichens have been used as biomonitors of ^{210}Po and ^{210}Pb atmospheric deposition in the vicinity of coal–fired power plants [17]. Despite the fact that mosses and lichens are commonly used in monitoring programs, the amount of data regarding to transfer of radionuclides to these organisms is limited, in particular with regard to natural radionuclides [18].

The aim of the study was to assess the relationship between the extent of air pollution with radioisotopes: ^{40}K, ^{137}Cs, ^{210}Pb and the distance from the cement plant.

Materials and methods

In the studies moss of the species *Pleurozium schreberi* were used, due to their prevalence in the Poland and frequent use for contamination bioindication. About a month before an exposure, samples of moss were picked in the forests of the Karkonosze Mountains, an area not significantly polluted, at a minimum distance of about 100 m from the main roads.

In the laboratory, mosses were manually cleaned, carefully mixed together, air-dried and the initial activity concentrations of radionuclides such as ^{40}K, ^{137}Cs and ^{210}Pb were determined using gamma-spectrometer. Then mosses were divided into 8 parts of 55 g each. All samples were packed in a plastic mesh net with mesh size of 1.5 × 1.5 cm, which was arranged in three-dimensional cylindrical boxes enabling uniform deposition efficiency of the analyzed elements from all directions. The test used two types of moss bags. In the A option, only mosses filled the volume of a bag, but in the B option, an additional plastic extender was located in the middle of the bag and mosses filled the space between it and bag walls. In Fig. 1 and 2 construction of the moss bags is shown.

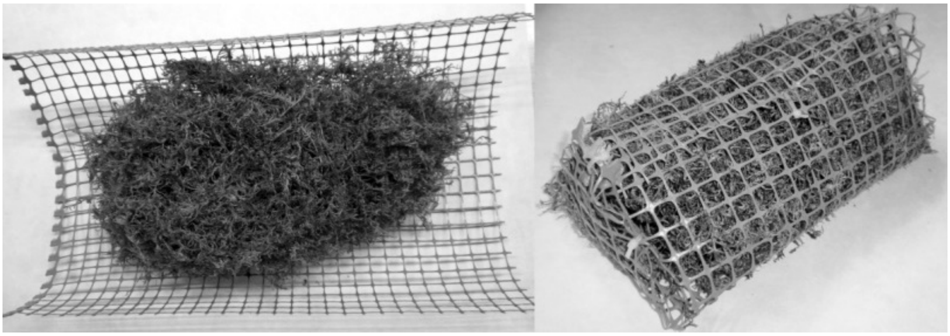

Fig. 1. Example of a moss bag, A option

Fig. 2. Example of a moss bag, B option

Moss bags were exposed in the study area between Chorula and Gorazdze villages, about 20 km far from Opole. The study area was located near the cement plant and limestone quarry connected by a conveyor transporting output from the quarry to the cement plant. For the study four sampling sites were selected. The first one was located about 100 m far from the road encompassing a cement plant and 200 m from a conveyor. Each subsequent sampling site was arranged about 400 m away from the previous and at the same distance from the conveyor as the first one. All samples were hanged in the branches of trees at a height of about 2 m. In each sampling site on the same tree two different options of moss bags were placed. After 98 days of field monitoring moss bags were collected and transported to the laboratory, in which they were treated in the same way like before the exposure.

The determination of radionuclide activity concentration in moss samples were carried out by means of a gamma-spectrometer with a germanium detector HPGe (Canberra) of high resolution: 1.29 keV (FWHM) at 662 keV and 1.70 keV (FWHM) at 1332 keV. Relative efficiency: 21.7 %. Energy and efficiency calibration of the gamma-spectrometer was performed with the standard solutions type MBSS 2, which covers an energy range from 59.54 keV to 1836.06 keV. The geometry of the

Fig. 3. Scheme of the study area

calibration source was a Marinelli container (447.7 ± 4.5 cm^3), with density 0.99 ± 0.01 g/cm^3, containing ^{241}Am, ^{109}Cd, ^{139}Ce, ^{57}Co, ^{60}Co, ^{137}Cs, ^{113}Sn, ^{85}Sr, ^{88}Y and ^{203}Hg. The geometry of sample container was Marinelli of 450 cm^3, and it was filled with about 50 g of moss. The time of measurement was about 24 hours for all moss samples. Measuring process and analysis of spectra were computer controlled with the use of the software GENIE 2000.

The obtained results of radionuclide activity concentration in moss samples allowed to calculate the Relative Accumulation Factor (*RAF*), which values indicate an increase in analyte amount during exposition:

$$RAF = \frac{a_{1,i} - a_{0,i}}{a_{0,i}} \tag{1}$$

where: $a_{1,i}$ and $a_{0,i}$ are the activity concentration of the i-th radionuclide in mosses respectively after and before the exposure [Bq/kg d.m.]. On a *RAF* scale score 0 is no growth and 1 and 2 are respectively single and double amount increment of the analyte in the sample. For the *RAF* values, the maximum measurement uncertainties ΔRAF were calculated using the formula:

$$\Delta RAF = \sqrt{\left(\frac{a_{1,i}}{a_{0,1}^2}\,\Delta a_{0,i}\right)^2 + \left(\frac{1}{a_{0,i}}\,\Delta a_{1,i}\right)^2} \tag{2}$$

where: $\Delta a_{0,i}$ and $\Delta a_{1,i}$ are the measurement uncertainties of i-th radionuclide activity concentration in mosses respectively before and after their exposure [Bq/kg d.m.].

Linear correlation coefficients were calculated to assess the linear relationship between radionuclides *RAF* and the distance from the cement plant. It was computed using the "correlation coefficient" function in Excel.

The share of various radiation sources in the total ^{210}Pb activity concentration in mosses after exposure was also analysed. Excessive lead activity concentration a_e was calculated from the formula:

$$a_e = a_{1,\text{Pb-210}} - a_{0,\text{Pb-210},m} - a_{1,\text{Bi-214}} \tag{3}$$

where: $a_{1,\text{Pb-210}}$ and $a_{1,\text{Bi-214}}$ are the activity concentration of the respectively ^{210}Pb and ^{214}Bi in moss after exposure and $a_{0,\text{Pb-210,m}}$ is the mean value of ^{210}Pb activity concentration in moss before exposure.

Results and discussion

All tested radionuclides were determined in all samples before and after exposure.

Table 1

Activity concentration $a_{1,i}$ [Bq/kg d.m.] of radionuclides in moss before exposure with measurement uncertainties $\Delta a_{1,i}$ [Bq/kg d.m.]

Sample number	I		II		III		IV	
	$a_{1,i}$	$\Delta a_{1,i}$	$a_{1,i}$	$\Delta a_{1,i}$	$a_{1,i}$	$\Delta a_{1,i}$	$a_{1,i}$	$\Delta a_{1,i}$
^{40}K	282	33	62	11	94	27	79	22
^{137}Cs	31	2	18	1	14	2	17	2
^{210}Pb	436	132	204	51	323	118	230	90

The mean initial activities of radionuclides in mosses were:

a) 129 ± 23 Bq/kg d.m. of ^{40}K,
b) 20.0 ± 1.4 Bq/kg d.m. of ^{137}Cs,
c) 298 ± 98 Bq/kg d.m. of ^{210}Pb.

Radionuclides concentration activities for all samples after exposure in both options are presented in Table 2.

Table 2

Activity concentration $a_{1,i}$ [Bq/kg d.m.] of radionuclides in moss after exposure with maximum measurement uncertainties $\Delta a_{1,i}$ [Bq/kg d.m.]

Distance from the cement plant	100 m		500 m		900 m		1300 m	
	$a_{1,i}$	$\Delta a_{1,i}$	$a_{1,i}$	$\Delta a_{1,i}$	$a_{1,i}$	$\Delta a_{1,i}$	$a_{1,i}$	$\Delta a_{1,i}$
A option								
^{40}K	220	31	196	32	221	30	211	20
^{137}Cs	35.2	2.5	30.6	2.4	51.6	2.8	36.7	1.5
^{210}Pb	588	129	500	138	679	142	549	102
B option								
^{40}K	211	32	162	27	166	32	178	23
^{137}Cs	30	2.4	27	2.0	31.7	2.7	22.0	1.5
^{210}Pb	587	144	495	122	490	138	410	102

In all samples post-exposure activities of ^{40}K, ^{137}Cs and ^{210}Pb were higher than mean pre-exposure activities. Relationship between the calculated *RAF* values and distance from the plant are shown in Fig. 4, 5.

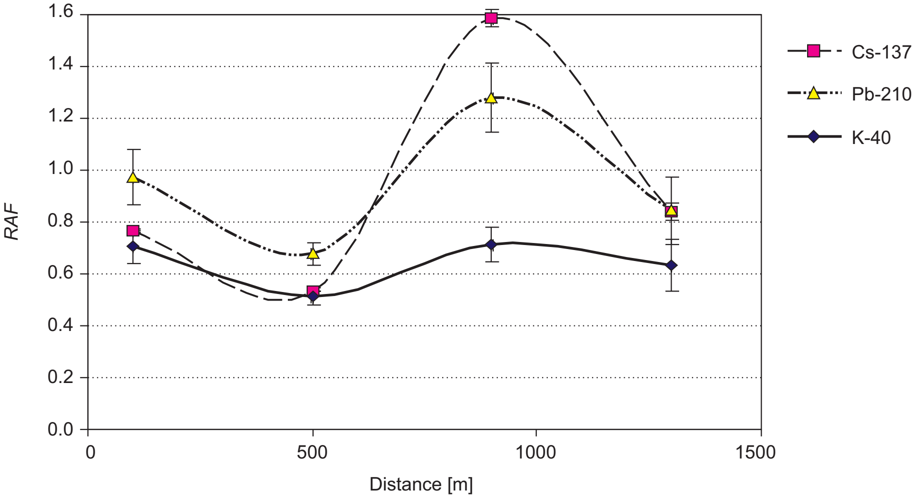

Fig. 4. *RAF* values for ^{40}K, ^{137}Cs and ^{210}Pb in moss bags A options

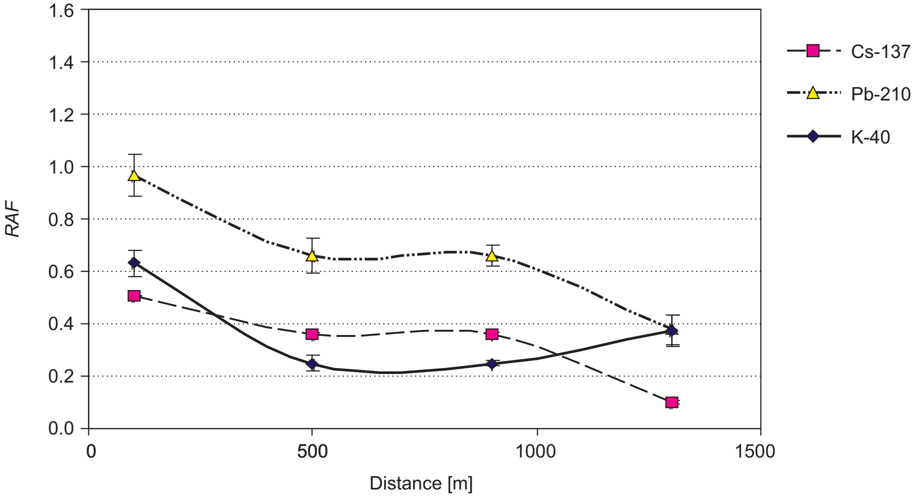

Fig. 5. *RAF* values for ^{40}K, ^{137}Cs and ^{210}Pb in moss bags B options

In A option, the biggest ^{137}Cs and ^{210}Pb activity concentration increases were observed at a distance of 900 m from the cement plant. The activity concentrations ratios were respectively 1.6 and 1.3. It does not coincide with B option, for which it was reached at a distance of 100 m from the cement plant, respectively with ratios 0.5 and

1.0. Similar differences in the *RAF* values in both options is observed for the smallest activity concentration increase of these radioisotopes, but in distances of 500 m (A variant) and 1300 m (B variant). Due to the divergence in trends between options it is difficult to determine relationship between activity concentration and distance. In opposite, the increase in ^{40}K activity concentration in both options is almost constant in all sampling sites.

In order to confirm the preliminary observations linear correlation coefficients were calculated. Correlation coefficients between the radionuclides *RAF* and the distance from the cement plant are:

- ^{40}K in A option – 0.03 and in B option – 0.55,
- ^{137}Cs in A option – 0.36 and in B option – 0.93,
- ^{210}Pb in A option – 0.10 and in B option – 0.95.

These results showed a total lack of correlation between the studied variables in A option and both partial and almost complete correlation in B option. This observation confirmed lack of ability to assess the trends of radionuclides activity increases with the change in the distance from the cement plant. Studies concerning such relationship require additional data.

In Fig. 6 the shares of autogenous (natural lead) and allogeneic (excessive lead) [19] are illustrated.

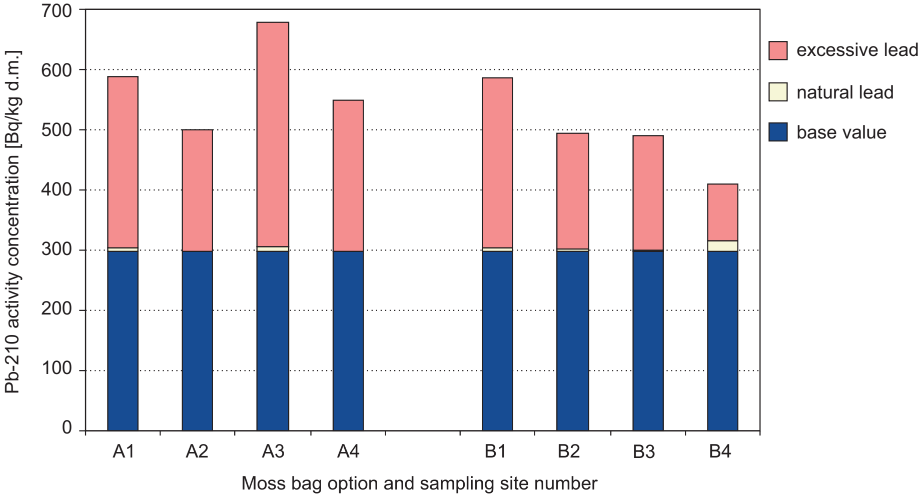

Fig. 6. The share of various sources of ^{210}Pb in his total activity

The ^{210}Pb activity concentration in moss after exposure is associated primarily with allogeneic component, representing the excess lead introduced into the environment due to human activity. A possible source of this radioisotope is the nearby cement plant. Minerals, raw materials and fuels used in the cement industry contain natural radionuclides. Due to the high temperatures during a cement production and large scale of the process, a significant release of radionuclides, including ^{222}Rn, ^{210}Po or ^{210}Pb to the atmosphere can be expected [1].

Conclusions

Substantial discrepancies of results in options disabled description of the relationship between increase in activity concentration of ^{40}K, ^{137}Cs and ^{210}Pb in mosses and the distance from the cement plant. No significant linear dependence in radionuclides deposition on the distance from the cement plant was observed.

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OCENA STANU ZANIECZYSZCZENIA POWIETRZA WYBRANYMI RADIOIZOTOPAMI W POBLIŻU CEMENTOWNI Z UŻYCIEM WORECZKOWEJ METODY

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Abstrakt: Przemysł wydobywczy i przetwórczy stanowi potencjalne źródło izotopów promieniotwórczych zanieczyszczających najbliższe środowisko. W celu oceny stanu środowiska w okolicy cementowni zastosowano metodę woreczkową z mchami. Celem doświadczenia było zbadanie zależności pomiędzy stopniem zanieczyszczenia powietrza ^{40}K, ^{137}Cs i ^{210}Pb a odległością od cementowni. Przeanalizowano również udział różnych źródeł promieniowania w sumarycznej aktywności ^{210}Pb w mchach po ekspozycji. Punkty pomiarowe zlokalizowane były w lesie niedaleko Opola, w jednej linii i w różnych odległościach od cementowni. W badaniu wykorzystano dwa typy woreczków wywieszone jednocześnie w tych samych miejscach. Zmierzono aktywność izotopów gamma-promieniotwórczych w próbkach mchów przed i po ekspozycji, wykorzystując gamma spektrometr z detektorem germanowym. Z uzyskanych wyników wyliczono względne współczynniki akumulacji (*RAF*). Chcąc ocenić w jakim stopniu aktywność radionuklidów zależy od odległości od cementowni, wyznaczono współczynniki korelacji liniowej. Ze względu na znaczną rozbieżność wyników w wariantach trudno jest ocenić trend wzrostu aktywności radionuklidów wraz ze zmianą odległości od cementowni. Nie zauważono wyraźnych zależności wielkości depozycji radionuklidów od odległości od cementowni.

Słowa kluczowe: względny współczynnik akumulacji (*RAF*), radioizotopy, metoda woreczkowa, cementownia

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COMPARATIVE STUDIES ON DECOMPOSITION OF SELECTED ESTROGENS AND XENOESTROGENS BY PHOTOCATALYSIS PROCESSES

BADANIA PORÓWNAWCZE ROZKŁADU WYBRANYCH ESTROGENÓW I KSENOESTROGENÓW W PROCESIE FOTOKATALIZY

Abstract: This study addressed the degradation efficiency of three different compounds belonging to the group of endocrine disrupting compounds (EDCs), namely 17β-estradiol (E2), 17α-ethinyl estradiol (EE2), and bisphenol A (BPA) in the photocatalysis process (UV/TiO_2). The subject of the study was a synthetic municipal waste water treatment plant effluent containing inorganic and optionally organic substances and to which the investigated micropollutants were added at a concentration of 500 μg/dm^3. The obtained results were compared in terms of the degradation of the selected compounds in deionized water. It was found that the efficiency of the photocatalysis depends significantly both on the environmental matrix and physico-chemical properties of the compounds present in the treated waste water. The highest degradation efficiency was observed for the synthetic effluent that contained only inorganic substances. The degradation of bisphenol A and 17α-ethinyl estradiol exceeded 90 % (after 60-minute irradiation) and 17β-estradiol was decomposed completely. The observed phenomenon can be attributed to the process termed as sensitized photocatalysis, which was enabled by inorganic substances present in the synthetic waste water. This phenomenon was not observed for the synthetic effluent that contained both inorganic and organic substances, and moreover the degradation efficiency of the micropollutans was lower. These observations were also confirmed by the results regarding the decomposition of the compounds in deionized water. In order to describe the course of photocatalytic oxidation reaction rate constants were determined as well as degradation half-lives using the Langmuir-Hinshelwood kinetic model.

Keywords: photocatalysis, micropollutants decomposition, bisphenol A, 17β-estradiol, 17α-ethinyl estradiol

Introduction

The increasing public awareness and the threat associated with the presence of contaminants in surface waters contributed to a significant increase in interest in new technological solutions aimed at efficient treatment and protection of global water

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resources. At the same time these solutions should be relatively efficient, cheap and meet a number of principles of green chemistry. An example of such a solution is heterogeneous photocatalysis carried out using titanium dioxide as a catalyst in this process (UV/TiO_2). This photochemical process is classified as one of the advanced oxidation processes (AOPs), in which the organic pollutants present in water are degraded into simpler compounds, and usually to CO_2 and H_2O as the final step of their mineralisation [1–5].

In the photocatalysis process, a catalyst with semiconducting properties (in this case, TiO_2) is subjected to irradiation with energy equal to at least band gap energy (E_G) and as a result the absorbed photon (hő) causes the transfer of an electron (e^-) from the valence band (VB) to the conduction band (CB) to form an electron hole (h^+), which is an unoccupied energy level. The resulting electron hole behaves as a positive electrical charge carrier [6–8]. Photosensitization of the semiconductor is schematically shown in Fig. 1 [9, 10].

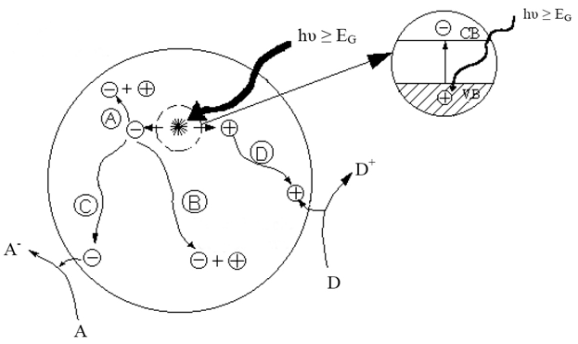

Fig. 1. TiO_2 photo excitation scheme: A) surface recombination freight, B) recombination volume of cargo, C) reduction of acceptor, D) oxidation of donor [9]

The electrons present on the surface of the semiconductor contribute to reduction of the acceptor group (step C), and a positively charged electron hole h+ is responsible for the oxidation of the donor group (step D). In this manner, the generated charge carriers (e–h^+) may also be subjected to recombination. In the semiconductor molecule one can distinguish two types of recombination: volume (step B) and surface (step A) recombination. The process of recombination competes with the transfer of charge to compounds that have been absorbed on the semiconductor surface [9–11]. It should be noted, that if the process of photocatalytic decomposition of organic pollutants occurs in aqueous solution it is also accompanied by chemical reactions that play a significant role in the process of photocatalysis. This is because the generated electron hole reacts with water molecules to generate hydroxyl radicals with a very high redox potential (+2.76 V) [12].

Currently, the UV/TiO_2 photocatalysis process is very often used to remove poorly biodegradable micropollutants, for which the conventional methods of water and wastewater are not fully effective. According to many authors [13–18] the application photocatalysis process using TiO_2 can allow for the removal of micropollutants in the range of approx. 70–98 %. For example, Heather et al [16] showed that the concentration of 17β-estradiol (natural estrogen) in the photocatalysis carried out using TiO_2 immobilized on Ti-6Al-4V alloy (catalyst loading of 1.5 mg/cm^2) after 3.5 hour exposure time was reduced by about 98 %. However, as reported by Cardoso da Silva et al [17] in the case of bisphenol A (xenoestrogen) the application of the UV/TiO_2 process (TiO_2 dose of 120 mg/dm^3) allowed for 77 % removal of this compound after 2-hour exposure time. The results of these experiments indicate that, the efficiency of the photocatalysis using TiO_2 depends both on the exposure time and the properties of the compound to be removed.

Based on the above-mentioned information, the present study assessed the efficiency of the degradation of three endocrine-disrupting compounds (EDCs): 17β-estradiol (E2), 17α-ethinyl estradiol (EE2) and bisphenol A (BPA), in an artificial municipal wastewater treatment plant effluent in the UV/TiO_2 process. The studied compounds differed primarily in terms of their origin and solubility in aqueous solution. The artificial municipal wastewater treatment plant effluent used in this study contained inorganic substances and, optionally, organic substances. The investigated micropollutants were added to this artificial effluent at a concentration of 500 μg/dm^3. The obtained results were compared for the decomposition efficiency of the selected compounds in deionised water. As a part of the study decomposition rate constants of the compounds in the UV/TiO_2 process were determined using the Langmuir-Hinshelwood kinetic model. Additionally, degradation half-lives of the investigated compounds were determined.

Materials and methods

The analytical standards of the studied compounds (17β-estradiol, 17α-ethinyl estradiol and bisphenol A) were purchased from Sigma-Aldrich (Poznan, Poland). The catalyst used was commercially-available titanium dioxide marked as P25 and purchased from Degussa. The dosage of titanium dioxide TiO_2 was 100 mg/dm^3. Methanol of >99.8 % purity and acetonitrile of >99.5 % purity were used in the study and were purchased from Avantor (Gliwice, Poland). For solid phase extraction (SPE) disposable Supelclean™ ENVI-18 cartridges with a volume of 6 cm^3 (1.0 g) and an SPE pressure chamber, both purchased from Supelco (Poznan, Poland), were used.

The solutions that were treated in the photocatalysis process were: (i) based on deionised water, (ii) prepared using the artificial effluent containing organic substances and inorganic substances, (iii) and prepared using the artificial effluent containing inorganic substances only with the addition of the investigated compounds in concentration of 500 μg/dm^3. Physico-chemical characteristics of the solutions used in this study are presented in Table 1.

The studied simulated final effluent containing bot organic and inorganic substances was prepared using dried nutrient broth, casein peptone, NH_4Cl, NaCl, $CaCl_2 \cdot 6H_2O$, $MgSO_4 \cdot 7H_2O$, K_2HPO_4 and KH_2PO_4. The other effluent was prepared without the

Table 1

The physical and chemical characteristics of the investigated solutions including EDCs

Treated solution	pH* [-]	Conductivity [μS/cm]	Absorbance (UV_{254}) [1/cm]
Deionised water	7.0	0.518	0.000
Simulated effluent containing inorganic substances		0.522	0.005
Simulated effluent containing organic and inorganic substances		0.793	0.055

* Adjusted with of 0.1 mol/dm^3 hydrochloric acid HCl solution or 0.1 mol/dm^3 sodium hydroxide NaOH solution.

addition of organic substances. Multiparameter inoLab® 740 meter manufactured by WTW (Wroclaw, Poland) was used for the pH and conductivity measurements. The absorbance was measured at a wavelength of 254 nm using UV-VIS Cecil 1000 spectrophotometer from Analytik Jena AG (Poznan, Poland).

The photolysis process was performed at 20 °C in a batch reactor from the Heraeus Company (Warszawa, Poland) with a volume of approx. 600 cm^3 and fitted with a 150 W medium-pressure immersion lamp. The photolysis process was carried out continuously for 60 minutes.

In order to determine the studied EDCs by HPLC-UV, 100 cm^3 (pH = 7) water samples of the tested compounds were extracted by solid phase extraction (SPE). The cartridge packing prior to extraction was conditioned with 5 cm^3 of acetonitrile and 5 cm^3 of methanol and next it was washed with 5 cm^3 of deionised water. The extracted compounds were eluted with 1 cm^3 of acetonitrile/methanol mixture (40/60, v/v).

The qualitative analysis of the extract was performed using the HPLC system from Varian (UV detector, wavelength 235 nm). The chromatographic separation was carried using Microsorb 100 C18 column with a length of 25 cm, a diameter of 4.6 mm and a pore size of 5 μm. The mobile phase was acetonitrile purchased from POCH.

The applied analytical procedure is characterised by the EDCs recovery in the range of 66 % (bisphenol A) and 78 % (17β-estradiol and 17α-ethinyl estradiol), which was determined for deionised water with the addition of analytical standards of the studied compounds at 500 μg/dm^3 (100 cm^3 volume of the sample).

Based on the literature data [19–22] the kinetics of the photocatalytic oxidation were described using the Langmuir-Hinshelwood model (LH). The following equation (1) gives the interpretation of the kinetics of the process, in which the concentration of oxidized micropollutants is a function of time: where:

$$r = \frac{dC}{dt} = k\left(\frac{KC}{1+KC}\right) \tag{1}$$

where: r – degree of oxidation of organic compounds;
C – concentration;
t – time;
k – rate of the oxidation reaction;
K – adsorption equilibrium constant.

Assuming that the oxidation of compounds in the process of photocatalysis is a pseudo first-order reaction, the rate constant can be calculated as the negative slope of the linear regression using equation 2:

$$-\ln\left(\frac{C_0}{C_t}\right) = kt \tag{2}$$

where: C_0/C_t – concentration of the organic compounds at time t = 0 and time t.

The half-life time $t_{1/2}$ was determined using equation:

$$t_{1/2} = \frac{\ln(2)}{k} \tag{3}$$

Results and discussion

Figure 2 shows the relationship between the time of irradiation and the decrease in the concentration of the EDCs in the photocatalysis process for the solution prepared using deionised water. It was determined that the concentration of 17β-estradiol, 17α-ethinyl estradiol and bisphenol A was decreasing with increasing irradiation time. The greatest reduction in the concentration of the compounds (approx. 35 % of the initial concentration) was observed in the initial irradiation time, this is, up to 10 minutes. After 10 minutes the elimination of 17α-ethinyl estradiol, 17β-estradiol and bisphenol A was approx. 80 %, 78 %, and only approx. 30 %, respectively. After 60

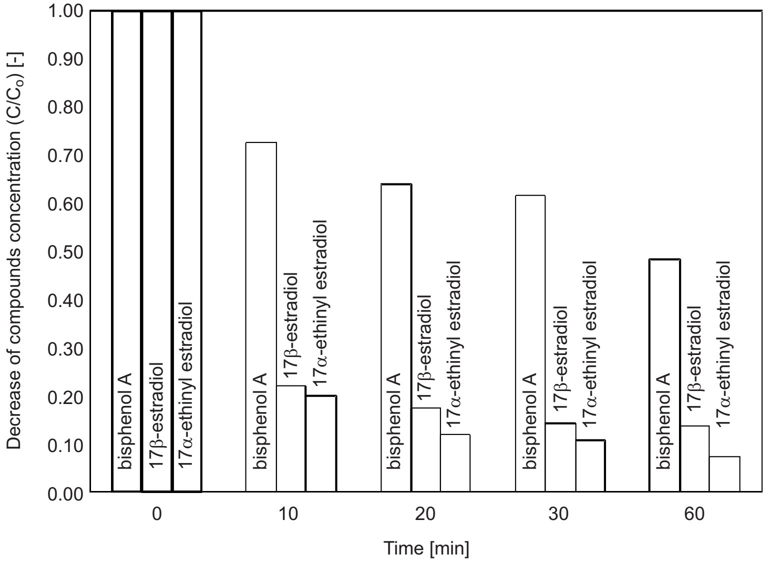

Fig. 2. The influence of radiation time on the decrease of EDCs concentration in UV/TiO_2 process of the deionized water

minutes of the process the concentration of bisphenol A was reduced below 50 %, whereas for the other two compounds the decomposition efficiency exceeded 93 %. The observed differences in the efficiency of the decomposition of the micropollutants can be associated with their physico-chemical properties. For example, the solubility of bisphenol A in water is 120 mg/dm^3, and for 17β-estradiol it is 3.90 mg/dm^3 [23, 24]. The investigated compounds are also different in terms of the logK_{ow} value, vapor pressure and Henry coefficient.

In the next stage of the study, the artificial effluent prepared using deionised water and containing only inorganic substances (Fig. 3) was subjected to the studied treatment process. It was observed that the degree of decomposition of all the compounds increased as compared to the results obtained for the process of UV/TiO_2 carried out using deionised water (Fig. 2). After 10 minutes of exposure the degree of degradation of 17β-estradiol, 17α-ethinyl estradiol and bisphenol A was 90 %, 88 % and 85 %, respectively. The greatest difference in the decomposition efficiency in comparison to the previous step of the study was obtained for bisphenol A (the decomposition efficiency was 2.5-higher). Despite further irradiation of the solution the concentration of 17β-estradiol and bisphenol A remained at a similar level, whereas after 60 minutes of the process, complete decomposition of 17β-estradiol was observed.

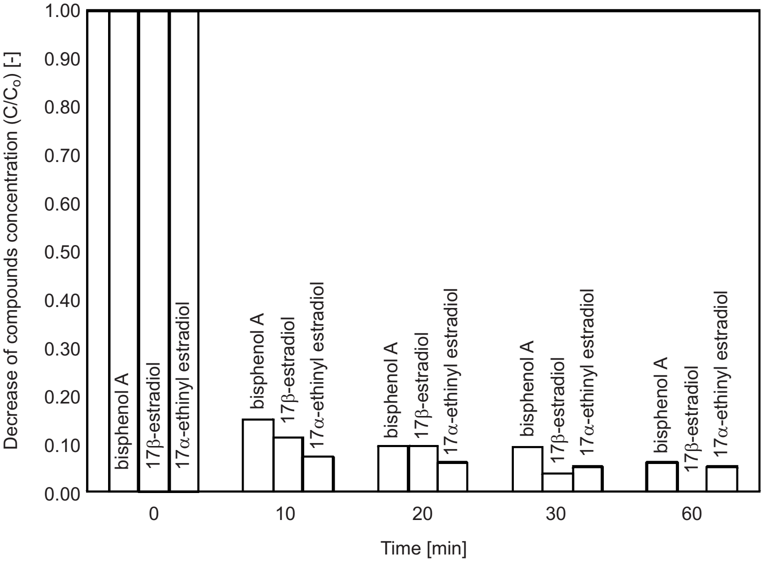

Fig. 3. The influence of the radiation time on EDCs decomposition in UV/TiO_2 process of the of simulated effluent containing inorganic substances

The observed higher degree of decomposition of the investigated compounds in the artificial effluent containing inorganic substances as compared to the deionised water may be due to the fact that the effluent contained substances allowing for the so-called sensitized photocatalysis to occur. As a result of visible radiation the molecule of inorganic chemical substance adsorbed on the semiconductor surface becomes excited.

Subsequently, the transfer of an electron from a chemical substance to the conduction band of the catalyst occurs with simultaneous generation of cation radical B^{+}. The resulting cation can further react, which may lead to complete degradation of the pollutants present in the solution. The substance that causes this phenomenon is referred to as sensitizer [25, 26]. Figure 4 shows the difference in the photocatalytic oxidation occurring a) with and b) without photosentization.

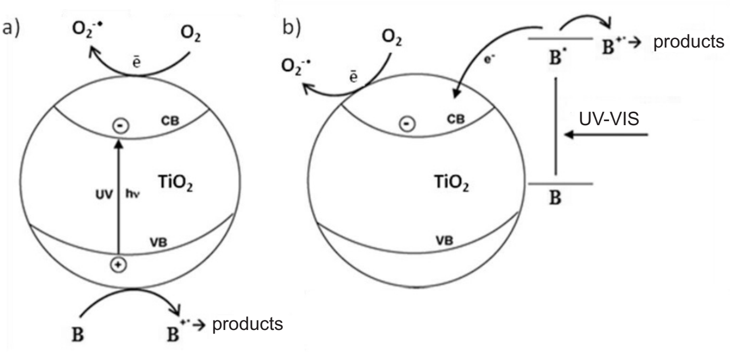

Fig. 4. The mechanism of the catalytic photooxidation a) with and b) without photosensitising

In the final stage of the study, the efficiency of the decomposition of the EDCs in the photocatalysis process was compared using the artificial effluent model effluent containing both organic and inorganic substances (Fig. 5). It was shown that the

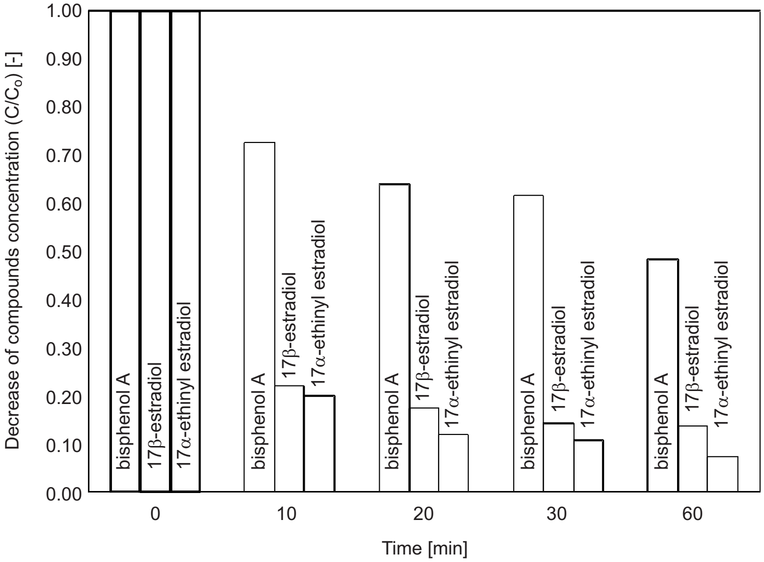

Fig. 5. The influence of the radiation time on EDCs decomposition in UV/TiO_2 process of the of simulated effluent containing organic and inorganic substances

reduction in the concentration of the compounds in this solution was lower than in the artificial effluent containing only inorganic substances and higher than for the solution prepared using deionised water. After 10 minutes of exposure the decomposition of 17β-estradiol, 17α-ethinyl estradiol and bisphenol A was 88 %, 60 % and 34 %, respectively. Further irradiation did not have a significant impact on the degradation of the micropollutants. This confirms earlier observations associated with the phenomenon of photosensibilisation. The obtained results show also that organic substances can inhibit the process of photocatalysis. It should be noted that the efficiency of the photocatalysis process depends on many factors such as pH and physico-chemical composition of the solution, concentration of the contaminant or the properties of the reagent [27].

Table 2 shows the degradation half-lives for the investigated EDCs in the UV/TiO_2 process, and the reaction rate constants determined based on the kinetics of the Langmuir-Hinshelwood for all the matrices tested. To determine the process kinetics data points from within the time range of 0 to 30 min. were selected.

Table 2

Reaction rate constant and decomposition half-lives of investigated EDCs obtained for the photolysis process

Matrices	EDC	Reaction rate constant [min^{-1}]	Coefficient of determination R^2 [-]	Half life of the compound [min]
Deionised water	bisphenol A	0.0108	0.87	51.4
	17α-ethinyl estradiol	0.0725	0.81	3.9
	17β-estradiol	0.0615	0.79	5.0
Simulated effluent containing inorganic substances	bisphenol A	0.1185	0.89	3.8
	17α-ethinyl estradiol	0.1409	0.80	2.1
	17β-estradiol	0.0998	0.86	1.0
Simulated effluent containing organic and inorganic substances	bisphenol A	0.0117	0.76	41.6
	17α-ethinyl estradiol	0.0668	0.80	8.3
	17β-estradiol	0.0841	0.76	2.4

In all the investigated cases the coefficient of determination R^2 was higher than 0.76, which indicates a good fit of measurement points to the model. The results show that the decomposition rate of all the EDCs in the photocatalysis process are the highest for the effluent containing only inorganic substances. These values are in the range of approx. 0.1 min^{-1} for 17β-estradiol to more than 0.14 min^{-1} for 17α-ethinyl estradiol. In the other two tested matrices the oxidation reaction rate constants for hormones (17β-estradiol and 17α-ethinyl estradiol) are about 7-fold higher compared with the value of this parameter determined for bisphenol A. The determined decomposition half-lives for the EDCs are the shortest (from 1 min for 17α-ethinyl estradiol to approx. 4 min for bisphenol A) in the case of treating the effluent containing only inorganic substances and the longest for the solution prepared using deionised water (4 min for the 17α-ethinyl estradiol to over 50 min to bisphenol A). Based on the obtained results it can therefore be concluded that 17β-estradiol and 17α-ethinyl estradiol are relatively well susceptible to degradation in the UV/TiO_2 process, as opposed to bisphenol A.

The obtained values of the oxidation rate constants and degradation half-life determined based on the kinetics of the Langmuir-Hinshelwood model are within the range reported in the literature [19–23, 28] regarding photocatalytic oxidation of organic substances other than the investigated EDCs. It should be noted that the value of these parameters is also affected by other process factors. For example Morteza et al in [28] determined that the value of the decomposition rate constant for the synthetic emerald green dye (this is one of the major dyes in the printing industry, but also used as an additive in poultry feed in order to inhibit the growth of mold, fungi and other parasites because of its toxic properties [29]) in the UV/TiO_2 carried out in solution at neutral pH (pH = 7) was 0.0330 min^{-1}, and at alkaline (pH = 9) it increased by one order of magnitude to a value of 0.1320 min^{-1}. Moreover, in the previous studies [30] it was found that the rate constants for the oxidation of organic substances depend also on the catalyst concentration. Oxidation reaction rate constants both for zearalenone (a substance belonging to a group of toxins produced by fungi of the genus *Fusarium*) and humic acids (natural contaminants in surface waters) were 3 and 10 times higher, respectively when the dose of the catalyst (TiO_2) increased 10-fold during the photocatalytic oxidation process.

Conclusions

Based on studies on the elimination of some of the compounds belonging to the group of EDC it was demonstrated that the efficacy of the process of UV/TiO_2 is significantly affected by both the type of environmental matrix and the physicochemical properties of the compound to be removed. The highest degrees of decomposition were obtained during the treatment of artificial effluent that contains only inorganic materials. In this case, the decomposition of bisphenol A and 17α-ethinyl estradiol exceed 90 % (after 60-minute exposure time) and 17β-estradiol was decomposed completely. The observed phenomenon can be explained by the presence of inorganic substances in the artificial effluent, which enabled the so-called sensitized photocatalysis. This phenomenon was not observed in the case of the effluent containing both inorganic and organic substances, and the degradation efficiency of the micropollutants was lower. These observations were also confirmed by the results obtained for the decomposition of the investigated compounds in deionised water. On the basis of he obtained results it was also found that 17β-estradiol and 17α-ethinyl estradiol are relatively well susceptible to degradation in the UV/TiO_2 in contrast to bisphenol A. These compounds differ in terms of their solubility in water which for the investigated sex hormones is approx. 30-fold lower than that of bisphenol A. The applied Langmuir-Hinshelwood model isotherm as a description of the UV/TiO_2 process allowed determination of the rate constants and degradation half-lives time for the studied EDCs. The determined parameters were the basis for a comparison of the obtained results with the results of other researchers.

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BADANIA PORÓWNAWCZE ROZKŁADU WYBRANYCH ESTROGENÓW I KSENOESTROGENÓW W PROCESIE FOTOKATALIZY

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Abstrakt: W ramach pracy podjęto badania nad oceną efektywności rozkładu trzech różnych związków należących do grupy substancji zakłócających procesy hormonalne (z ang. Endocrine Disrupters Compounds EDCs), tj. 17β-estradiol (E2), 17α-etynyloestradiol (EE2) oraz bisfenol A (BPA) w procesie fotokatalizy (UV/TiO_2). Przedmiotem badań były modelowe odpływy z oczyszczalni ścieków bytowych zawierające substancje nieorganiczne i opcjonalnie organiczne, do których dodawano badane mikrozanieczyszczenia w stężeniu 500 μg/dm^3. Uzyskane wyniki badań porównano pod katem skuteczności rozkładu wybranych związków dla wody zdejonizowanej. Wykazano, że na skuteczność procesu fotokatalizy istotny wpływ ma zarówno rodzaj matrycy środowiskowej, jak i właściwości fizykochemicznych usuwanych związków. Najwyższe stopnie rozkładu uzyskano podczas oczyszczania odpływu modelowego zawierającego wyłącznie substancje nieorganiczne. Rozkład bisfenolu A oraz 17α-etynyloestradiolu przekraczał wówczas 90 % (po 60-minutowym czasie naświetlania), a 17β-estradiol został rozłożony całkowicie. Zaobserwowane zjawisko można wytłumaczyć obecnością w ściekach modelowych chemicznych substancji nieorganicznych umożliwiających przebieg tzw. fotokatalizy sensybilizowanej. W przypadku odpływu modelowego zawierającego zarówno substancje organiczne, jak i nieorganiczne tego zjawiska nie obserwowano, a efektywność rozkładu mikrozanieczyszczeń była mniejsza. Powyższe obserwacje potwierdzają również uzyskane wyniki rozkładu związków dla wody zdejonizowanej. W celu opisu przebiegu fotokatalitycznego utleniania wyznaczono stałe szybkości reakcji oraz czasy połowicznego rozkładu posługując się kinetyką modelu Langmuira-Hinshelwooda.

Słowa kluczowe: fotokataliza, rozkład mikrozanieczyszczeń, bisfenol A, 17β-estradiol, 17α-etynyloestradiol

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INFLUENCE OF WATER MATRIX ON THE RETENTION OF PHARMACEUTICALS BY HIGH-PRESSURE MEMBRANE FILTRATION

WPŁYW MATRYCY WODNEJ NA RETENCJĘ FARMACEUTYKÓW W WYSOKOCIŚNIENIOWEJ FILTRACJI MEMBRANOWEJ

Abstract: High-pressure membrane processes, including nanofiltration and reverse osmosis, allow for the removal of a wide range of organic micropollutants (including pharmaceutical compounds) from water streams. Those processes also may be an effective method for in-depth treatment of water containing pharmaceutical compounds. The paper presents a comparison of retention of selected pharmaceuticals from the group of non-steroidal and anti-inflammatory drugs, *ie* ibuprofen and diclofenac and psychotropic drugs – carbamazepine, present in various aqueous matrices in the nanofiltration process. Deionized water based solutions as well as model and real wastewater effluents after biological treatment processes were subjected to the filtration process. The nanofiltration process was carried out in a cross-flow tubular membrane filtration system. Three polyamide membranes AFC30, AFC40 and AFC80 from PCI Membrane System Inc were used. It has been found, that the retention of pharmaceutical compounds increased with the membrane filtration time, regardless of the composition of the treated aqueous matrix. Moreover, the presence of inorganic compounds and high-molecular organic substances had a positive effect on the membrane separation process of micropollutants.

Keywords: diclofenac, ibuprofen, carbamazepine, nanofiltration

Introduction

The escalating problem of the presence of a wide range of pharmacological substances in the environment becomes one of topical research issues, which are currently being undertaken in the field of environment engineering and protection. Excessive consumption of medicines belonging to the group of biologically active substances may compromise the stability of many ecosystems, especially of water

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ecosystems [1]. The Directive of the European Parliament and of the Council 2013/39/EU of 12 August 2013 [2] ordered the monitoring of substances listed in the decision of the Executive Commission (EU) 2015/495 of 20 March 2015 [3]. Apart from nine other organic micropollutants includes diclofenac. That substance watch list includes, among others, pharmaceutical compounds from the group of non-steroidal and anti-inflammatory drugs – diclofenac and synthetic hormones – 17-alpha-ethinyl-estradiol. The data obtained during the monitoring will allow to determine whether these pharmaceutical compounds should be classified as one of the priority substances, and thereby force the need to develop methods for their effective elimination from the aquatic environment.

Among the unconventional methods, which allow for the treatment of water streams from a wide range of organic micropollutants, high-pressure membrane processes *ie* nanofiltration and reverse osmosis are mentioned. The effectiveness of those processes depends on many factors which include operating parameters of the process, the physicochemical properties of used membranes and removed compounds as well as on the chemical composition of the treated water matrix [4, 5].

The aim of the study was to determine the influence of the chemical composition of water matrices on the retention degree of pharmaceutical compounds from the group of non-steroidal and anti-inflammatory drugs – diclofenac and ibuprofen and psychotropic drugs – carbamazepine in the nanofiltration process. The high-pressure membrane filtration process was carried out in the cross-flow mode using a semi-industrial installation equipped with a tubular membrane module. Three types of polyamide membranes AFC30, AFC40 and AFC80 from PCI Membrane System Inc. (USA) were tested. In addition, a description of the separation mechanisms, which determine the retention of micropollutants was undertaken.

Materials and methods

The study on the effectiveness of the removal of pharmaceutical micropollutants in the nanofiltration process was carried out using three water matrices *ie* a solution prepared based on deionized water and a real and model effluent from a mechanical-biological wastewater treatment line (Table 1). To all water matrices selected patterns of micropollutants were added.

Table 1

Physicochemical characteristics of examined water solutions

Water matrix	Deionized water	Model effluent*	Real effluent
pH	7.00	7.10	7.15
Conductivity [mS/cm]	0.271	0.992	1.109
Absorbance (λ = 254 nm) [nm^{-1}]	0.038	0.064	0.269
TOC [mg/dm^3]	5.02	29.25	30.16

* The model effluent was prepared on the basis of tap water and dry nutrient broth, casein peptone, NH_4Cl, $NaCl$, $CaCl_2 \cdot 6H_2O$, $MgSO_4 \cdot 7H_2O$, K_2HPO_4 and KH_2PO_4.

The concentration of tested pharmaceutical compounds in water solutions was established at 1 mg/dm^3. Analytical standards of non-steroidal and anti-inflammatory drugs in the form of diclofenac (DCL) and ibuprofen (IBU) sodium salts and the psychotropic drug – carbamazepine (CBZ) were purchased from Sigma-Aldrich (Poznan, Poland) (Table 2).

Table 2

Characteristics of pharmaceutical micropollutants

Pharmaceutical compound	Diclofenac sodium salt	Ibuprofen sodium salt	Carbamazepine
Symbol	DCL	IBU	CBZ
Molecular formula	$C_{14}H_{10}Cl_2NNaO_2$	$C_{13}H_{17}O_2Na$	$C_{16}H_{12}N_2O$
Molecular weight [g/mol]	318.13	228.26	236.3
Solubility in H_2O [mg/dm^3]	50	100	17
pK_a	4.15	4.91	2.30
log K_{ow}	4.51	3.97	2.45
Stokesa radius [nm]	0.414	0.295	0.319

The nanofiltration process was operated in a cross-?ow mode using a semi-industrial installation TMI 14 from J.A.M INOX Produkt equipped with a tubular flow-through membrane module with a polyamide membrane from PCI Membrane System Inc. (USA) (Table 3). The membrane total surface area was 240 cm^2. The filtration process was conducted for 180 min to collect 20 % of the initial volume of the feed.

Table 3

Characteristics of used membranes

Membrane type	AFC30	AFC40	AFC80
Skin layer-material	polyamide	polyamide	polyamide
Molecular weight cut-off [Da]	200	200	< 200
NaCl retention [%]	75	60	80
$MgSO_4$ retention [%]	90	92	98
pH range	1.5–9.5	1.5–9.5	1.5–10.5
Hydrophilicity*	4	4	4

* 1 – low hydrophilicity, 5 – high hydrophilicity.

In the initial step of the study the impact of the transmembrane pressure on the transport properties of used membranes was assessed (Fig. 1). The volumetric permeate flux of deionized water free of pharmaceutical compounds was determined according to

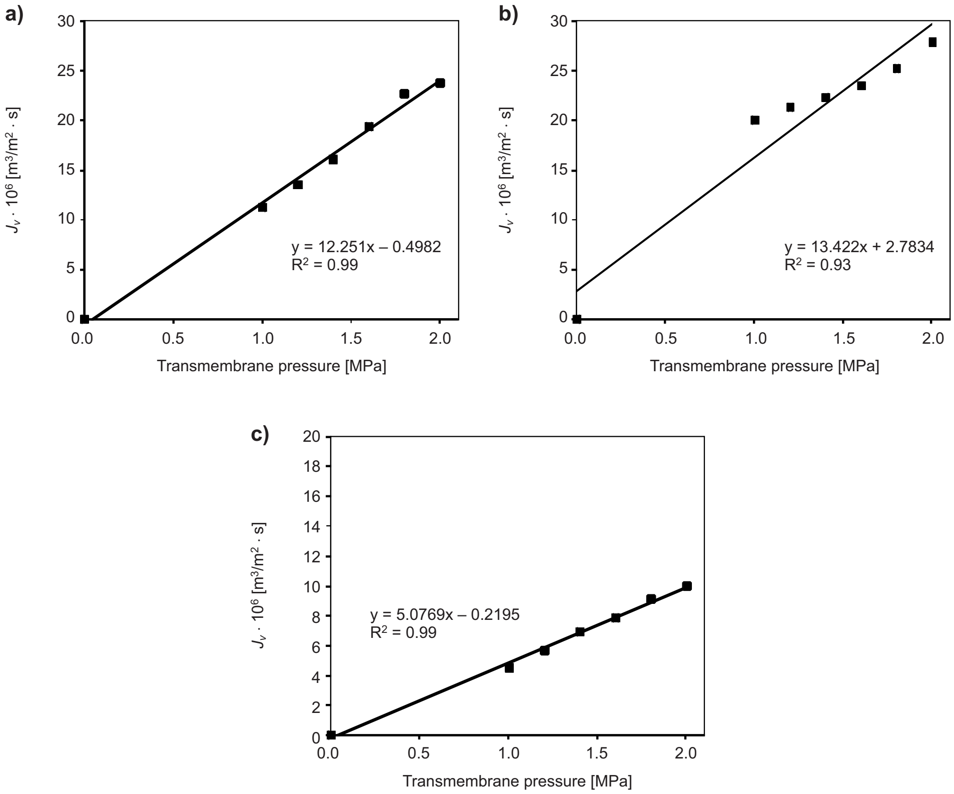

Fig. 1. Influence of transmembrane pressure on the value of the permeate volumetric flux (membrane a) AFC30, b) AFC40 and c) AFC80)

equation (1). The process transmembrane pressure used in the study was assumed at the level of 2 MPa.

$$J_v = \frac{V}{F \cdot t} \tag{1}$$

where: J_v – volumetric permeate flux [m^3/m^2 · s];
V – permeate volume [m^3];
F – membrane surface area [m^2];
t – filtration time [s].

The retention degree of pharmaceutical micropollutants, which was determined on the basis of equation (2), estimate the effectiveness of the process.

$$R = \left(1 - \frac{C_f}{C_0}\right) \cdot 100\,\% \tag{2}$$

where: R – retention degree [%];
C_p – pharmaceutical concentration in the permeate [mg/dm^3];
C_f – pharmaceutical concentration in the feed [mg/dm^3].

The concentration of the tested pharmaceuticals was examined by the use of HPLC chromatography combined with UV detection preceded by solid phase extraction SPE (sample preparation stage for chromatographic determination). During the SPE extraction disposable Supelclean ™ ENVI-8 columns (volume 6 cm^3 and 1.0 g phase) from Supelco (Poznan, Poland) were applied. In order to solvation the octylsilane (C_8) column bed was washed with 5 cm^3 of methanol and then conditioned with the same volume of deionized water at pH 7. Next water sample of a volume of 20 cm^3 was added to the extraction cartridge. After the extraction the column bed was dried under vacuum. The obtained extract was eluted with 3 cm^3 of methanol and subjected to drying in a stream of technical nitrogen. Prior to the chromatographic determination the eluent was dissolved in 0,1 cm^3 of methanol. For the analysis a Varian (Warszawa, Poland) high performance liquid chromatograph equipped with a Hypersil GOLD column from Thermo Scientific (Warszawa, Poland) with a length of 25 cm, a diameter of 4.6 mm and a pore size of 5 μm were used. A mixture of acetonitrile/water in the proportions of 85:15 (v/v) was applied as the mobile phase.

Results and discussion

Figure 2 shows the retention coefficient for the tested pharmaceutical micropollutants obtained during the filtration of the solution prepared on the basis of deionized water. With the increasing filtration time, the reduction in the concentration of micropollutants was observed. This tendency was particularly observed in the case of IBU by the use of AFC80 membrane. The retention coefficient of that pharmaceutical compound was about 27 % after 15 minutes of filtration and after 120 minutes, reached the value of 54 %, while after 180 minutes exceed 88 %. The observed tendency is not typical compared to the results presented in papers in this field, where the retention of micropollutants usually decreases with the time of membrane filtration [6]. In the case of examined pharmaceuticalsthis relationship might have been caused by the change of the charge of the membrane surface due to the deposition in the skin layer and in the pores of negatively charged DCL molecules ($pK_a = 4.15$), or neutral CBZ molecules ($pK_a = 2.30$).

Among factors affecting the retention of organic micropollutants the physicochemical properties of the removed of compounds should been mentioned next to the load of the membrane surface. This is connected with the coexistence of three different mechanisms, which are responsible for the separation of compounds in the nanofiltration process [7] *ie* the exclusion mechanism, resulting from the so-called spheric effect, the electrostatic repulsion and physicochemical interaction occurring at the same time between the micropollutants, compounds of the treated solution and the surface of the membrane. In the initial stage of filtration for the AFC40 and AFC80 membranes (respectively to 105 and 45 min), it was observed that the retention of pharmaceuticals depended on their molar mass, which refers to the spherical construction of each

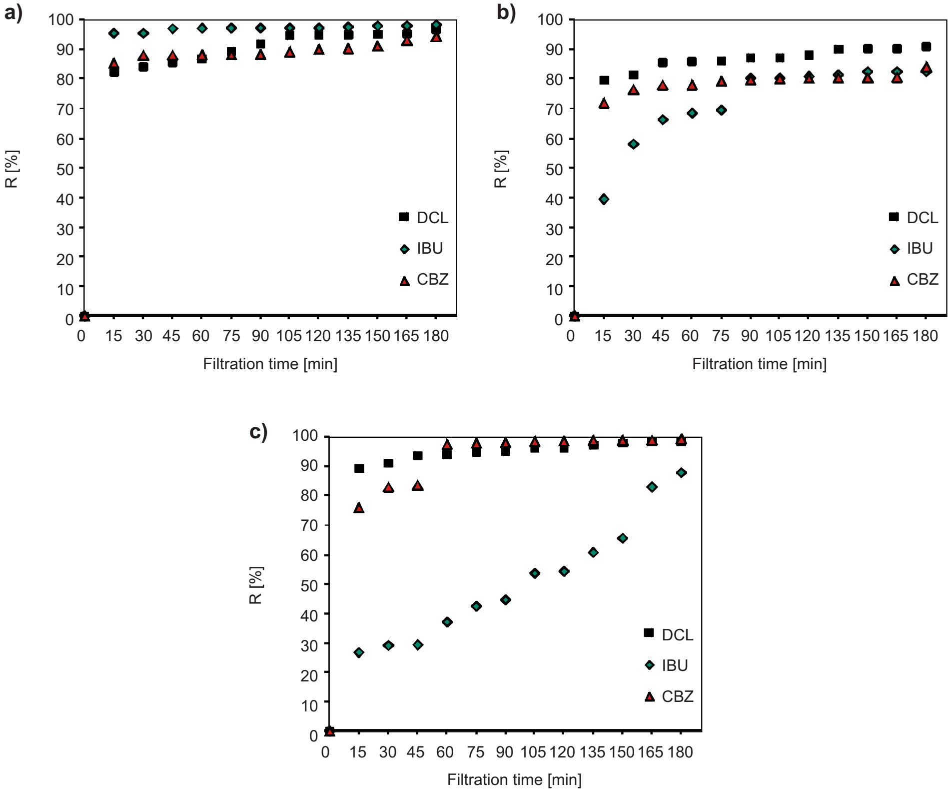

Fig. 2. Effect of the filtration time on the retention coefficient of deionised water spiked with pharmaceutical compounds (membrane a) AFC30, b) AFC40 and c) AFC80)

compound [8]. This dependence has also been confirmed by other researchers [9]. The highest removal degree in the process carried out by the use of the AFC80 membrane was observed for DCL (the retention coefficient after 45 minutes of filtration amounted to over 93 %) with a molecular weight equal to 318.13 g/mol and the lowest removal degree for IBU, which have a molecular weight of 228.26 g/mol (retention coefficient does not exceed 30 %). This demonstrates that the dominant mechanism of separation was the molecular sieving mechanism. On the other hand, during the continuation of the filtration so significant difference in the retention of examined pharmaceuticals were no longer observed. The determined retention values of DCL and CBZ were similar. This might be caused by the fact that both compounds are also characterized by a lower water solubility than the IBU. By contrast, the results presented in [10] indicated, that a low solubility of a compound in water indicates its high ability to be separate by the use of high pressure membrane processes. Therefore it can be assumed that at the subsequent stage of filtration the separation efficiency depended mainly on the exclusion mechanism (Table 2) and electrostatic repulsion, which is associated with the change of the membrane charge.

The molecular sieving mechanism also decided on the effectiveness of the process carried out using a AFC40 membrane. The highest removal degree was achieved for DCL (the retention coefficient after 180 minutes of filtration exceed 91 %), and the lowest for IBU, which amounted to around 82 %. For the AFC30 membranes it was observed, that the retention coefficient of micropollutants increases with the increasing pKa value of removed pharmaceuticals. The removal degree of negatively charged molecules of IBU (pK_a = 4.91) exceeded 98 %, while the CBZ molecules, which belonging to substance endowed with a neutral charge, were retained only in 94 %. It can be assumed, that the separation of pharmaceutical compounds by the use of a AFC30 membrane, which have a negative charge during the implemented process conditions (pH = 7), resulted from the Donnan exclusion mechanism.

In the next stage of the study the filtration of model (Fig. 3) and real effluent (Fig. 4) spiked with pharmaceutical patterns was undertaken. In the first 45 minutes of filtration the values of the retention coefficient of all three examined pharmaceutical compounds, which were present in both matrices, increased in comparison to those observed in the case of filtration of the deionized water matrix. For example, the retention degree of pharmaceutical agents after 45 minutes of filtration of the real effluent by the use of

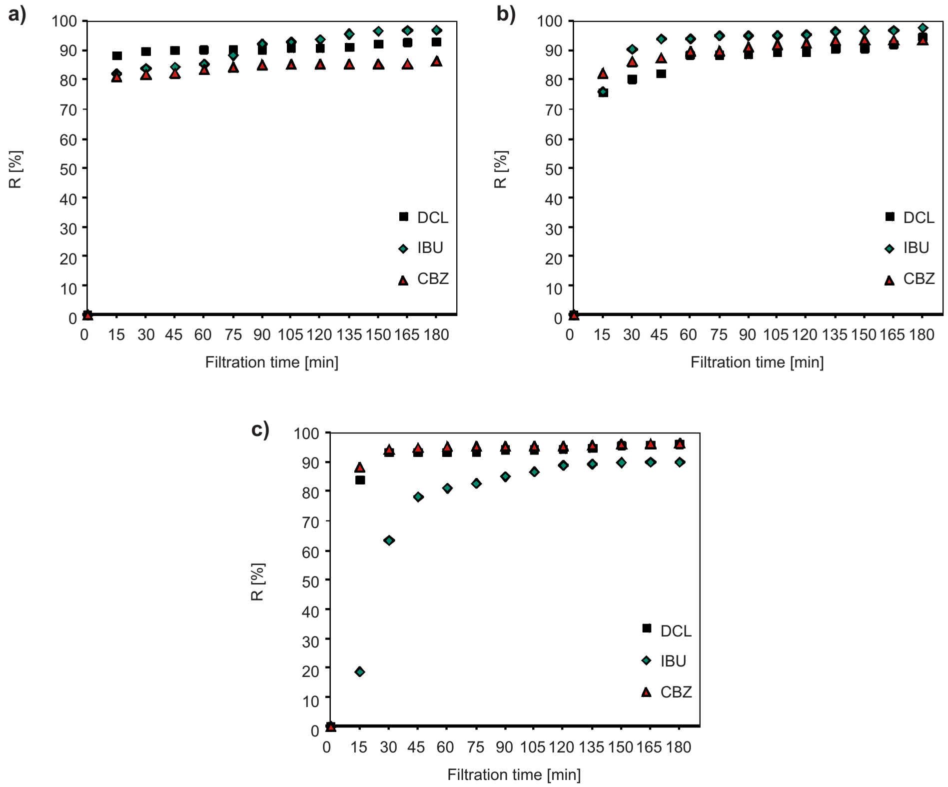

Fig. 3. The retention coefficient of drugs during the nanofiltration process of model wastewater effluent (membrane a) AFC30, b) AFC40 and c) AFC80)

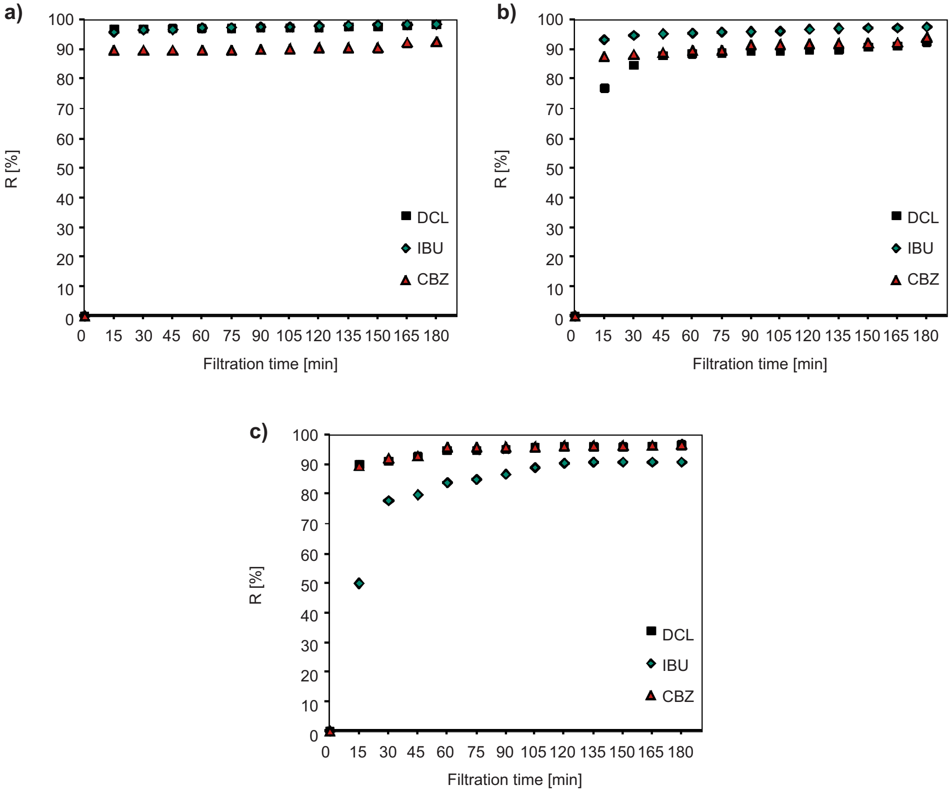

Fig. 4. The retention coefficient of pharmaceutical micropollutants during the nanofiltration process of real wastewater effluent (membrane a) AFC30, b) AFC40 and c) AFC80)

AFC80 membrane amounted respectively about 93 % for DCL and CBZ, and 80 % for IBU molecules. The retention of pharmaceutical compounds occurring in the real effluent after 15 minutes of filtration through the AFC30 membrane exceed 90 % and maintained at this level during 180 minutes of the process duration.

However the retention degree of DCL and CBZ designated for the AFC80 membrane between 60 and 180 minutes of filtration of both effluents received a relatively stable value, which exceeded 94 % for DCL and 95 % for CBZ. It should be emphasized that the retention of pharmaceuticals for the deionized water solution ranged from 75 % to 99 % depending on the type of the compound and filtration time. The reason for this phenomena may be the presence of inorganic compounds in the treated solution, particularly Ca^{2+} ions, which are able to reduce the charge of the membrane surface resulting in the reduction of the retention of negatively charged molecules of micropollutants [12]. It can be assumed that during the filtration of solution containing organic and inorganic substances (model and real effluent) the separation mechanism of pharmaceutical compounds was completely different than in the case of filtration of solution prepared based on deionized water.

The highest retention degree of DCL and IBU present in real effluent was reported for the AFC30 membrane and exceeded 98 %, whereas CBZ was most efficiently retained on the AFC80 membrane. The membrane, which allowed for the most effective separation of micropollutants from the deionized water solution was the AFC80 membrane. An exception was only the IBU retention coefficient, which was at the highest level for the AFC30 membrane, and adopts a value of about 98 %. The increasing retention of pharmaceutical compounds occurring in water matrices with different chemical composition relative to matrices prepared on deionized water can be attributed, especially in the initial filtration time to the ability of micropollutants to bind to functional groups of high-molecular-organic compounds and form of so-called macromolecular complexes, which are featured with a higher retention than single micropollutants [11]. The presence of high-molecular-weight organic compounds in solutions results in the formation of an additional filtration barrier in the form of a so-called secondary membrane on the membrane surface. This phenomenon leads to the increase of filtration resistance and consequently increases the retention degree of low-molecular-weight pharmaceutical compounds. The formation of a secondary membrane as a result of the fouling phenomenon was confirmed by the determination of the permeate volumetric flux, which in case of the filtration of model and real effluent decreased by more than 7 % regarding to the filtration efficiency obtained for deionized water (Fig. 5). Indirectly, it was also evidenced by the fact that the increase in IBU retention was much faster during filtration of model or real effluent (Fig. 3 and 4) than during the filtration of the solution based on deionized water (Fig. 2).

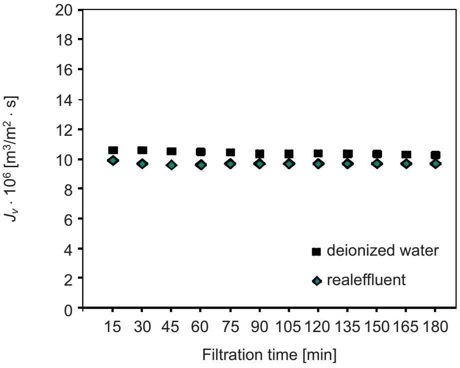

Fig. 5. Influence of water matrix on the value of the volumetric permeate flux (membrane AFC80)

Conclusions

The efficiency of the filtration process depended strictly on physicochemical properties of removed organic micropollutants, as well as on the membrane surface charge and the composition of the feed. In addition, type of the dominant separation mechanism was changing with the filtration time and the occurrence of the fouling phenomena, which typically occured during the membrane filtration.

With the filtration time, the reduction in the concentration of pharmaceutical micropollutants was observed. The retention degree of DCL and CBZ after 15 min of filtration of all tested matrices exceeded 76 %. In the case of IBU that value amounted about 50 % for the AFC80 membrane and increased with the filtration time and the increasing of the fouling phenomena.

The separation process of DCL and CBZ was most efficient in the case of filtration of deionized-water based solutions by the use of AFC80 membrane. However, the degree of IBU retention achieved the highest value during the filtration of the model effluent using AFC40 membrane. It can be assumed, that the presence of high-molecular organic substances resulted in the formation of so-called "secondary membrane" on the membrane surface, which contributes to improvement of the separation properties of low-molecular-weight organic micropollutants.

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WPŁYW MATRYCY WODNEJ NA RETENCJĘ WYBRANYCH FARMACEUTYKÓW W WYSOKOCIŚNIENIOWEJ FILTRACJI MEMBRANOWEJ

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Abstrakt: Wysokociśnieniowe procesy membranowe, do których zaliczamy nanofiltrację i odwróconą osmozę, pozwalają na oczyszczenie strumieni wodnych z szerokiej gamy mikrozanieczyszczeń organicznych. Mogą znaleźć również zastosowanie w doczyszczaniu wód pod kątem eliminacji związków farmaceutycznych. W pracy przedstawiono porównanie stopnia retencji wybranych farmaceutyków z grupy niesteroidowych leków przeciwbólowych i przeciwzapalnych, tj. ibuprofen i diklofenak oraz leków psychotropowych – karbamazepina, obecnych w różnych matrycach wodnych w procesie nanofiltracji. Oczyszczaniu poddano roztwory sporządzone na bazie wody zdejonizowanej oraz modelowy i rzeczywisty odpływ po biologicznym oczyszczaniu ścieków. Proces nanofiltracji prowadzono w układzie filtracji krzyżowej przy zastosowaniu rurowego modułu membranowego. Oceniono efektywność procesu przy wykorzystaniu trzech poliamidowych membrana, tj. AFC30, AFC40 i AFC80 firmy PCI Membrane System Inc. Określono, że wraz z czasem filtracji membranowej wzrasta stopień retencji badanych związków farmaceutycznych niezależnie od składu oczyszczanej matrycy wodnej. Ponadto stwierdzono, że obecność w roztworze związków nieorganicznych oraz wysokocząsteczkowych substancji organicznych wpływa korzystnie na proces membranowej separacji mikrozanieczyszczeń.

Słowa kluczowe: diklofenak, ibuprofen, karbamazepina, nanofiltracja

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THE INFLUENCE OF COCONUT FIBRE AND SALTS COMPOSITE USED FOR ELIMINATING SLIPPERINESS AND ON ROADS ON SOILS

WPŁYW KOMPOZYTU MIESZANKI WŁÓKIEN KOKOSOWYCH I SOLI STOSOWANYCH DO USUWANIA ŚLISKOŚCI JEZDNI NA GLEBY

Abstract: The subject of the study is analyzing the impact of coconut fibre and salt mixture used for eliminating slipperiness on roads on roadside soil. The tests were done on the soil samples taken from the fixed areas twice: in the autumn before applying the composite and in the following spring. Laboratory tests indicated decrease of conduciveness in soil after using the composite in wintertime. This can cause decreasing saltiness of roadside soil. In contrast to commonly used methods of eliminating slipperiness on roads with salts only applying the composite could diminish the negative effects of roadside soil saltiness.

Keywords: saltiness, eliminating slipperiness on roads, roadside soil, coconut fibre, easily soluble salts

Introduction

Saltiness is one of chemical soil pollution which has many reasons: from natural processes, the dispersion of fungicides or insecticides or fertilizer on growing crops to changes caused by substances directly introduced to environment by people.

The destructive force of soil saltiness is caused mainly by concentrating the soil which makes it hard for plants to absorb water and nutrient substances. Soil saltiness also changes the ionic balance of environment, soil characteristics and presence of toxic elements. The process can be noticed mainly in alkalization of soil environment [1].

One of the reasons of soil saltiness caused by people is using chemical substances for maintaining roads in wintertime. Salts like NaCl and $CaCl_2$ are commonly used for eliminating road slipperiness. The substances can spread on roadside soil increasing the

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area of soil saltiness [2]. This explains why using salts on the roads in wintertime has serious impact on the local areas.

Negative effects of using salts on roads were noticed in the 50s when the damage of "green areas" in urban locations was observed. It was the time when the studies and analysis of effects of using salts on roads were carried out. The analysis conducted in Warszawa by Dobrzanski et al indicated the negative effect of salt on the urban plants [3]. The authors of the study have shown almost complete saltiness of the soil caused by salt used on roads. During the following years similar studies were carried out in many Polish cities [4–7].

A lot of attention in the environmental studies was devoted on the impact of chemical substances on roadside plants. Czerniawska-Kusza et al (2004) conducted detailed observations: they indicated significant impact of NaCl on roadside trees in Opole [8]. The study was based on observing damages on the tree leaves and branches. It was concluded that the most damaged leaves accumulate sodium and chlorine the most.

Bach et al carried out a similar observation but in a different city – Krakow [4]. Tests made on roadside soil revealed soil saltiness and more specific changes in its composition that impacts the accessibility of microelements and quality and quantity of microorganisms.

The environmental effects of using salt on roads on the roadside soil are: relocating nutritious cations, decreasing soil penetrability and scattering soil colloids what is more, the ions of salt can draw heavy metal ions causing soil damage [9]. Both sodium and chlorine have considerable effect on nitrogen changes and decrease soils structure through reduction organic substances [10].

The awareness of negative impact of using salts for eliminating slipperiness on roads on the roadside soil shows the need of searching alternative methods of maintaining roads in wintertime. Nowadays, the most effective substances for eliminating slipperiness on roads used in big quantities can cause dramatic changes in roadside environment. Hence, an effective way of protecting roads from slipperiness which is also safer for environment is needed.

The aim of the studies in the this thesis was defining the physical and chemical changes of roadside soils after using the composite of coconut fibre and salt in wintertime and assessing the usefulness the composite.

Materials and methods

Coconut fibre (coconut chips) are fraction of crumbled coconut fruit. The main aim of coconut fibre is to maintain the surface of easily soluble salt (NaCl), which will react with frozen road surface. Lengthening the time of using the composite would help in dissolving the ice and snow on the road quickly and effectively. This technology would reduce the amount of used salt and would stop the salt on the road during the next applying process. What is more, coconut chips re close to neutral pH and it can help to save balance of roadside soil. The composite used for the tests was created from coconut fibre and salt mixed in weight proportion 1:10.

The tests of the impact of coconut chips and salt mixture were carried out on the roads among the fields. The exact location of the roads are: Obrowiec – Gogolin, Zakrzow – Zakrzow Osada, Kamien Slaski – Gogolin and Kosorowice – Kamien Slaski. On each of four test areas two zones were created: A and C – zones directly next to the road on the left and right and zones B and D adjacent to zones A and C. the zones were rectangular, sized 10 meters long and 1 meter wide (Fig. 1). Soil samples were taken on

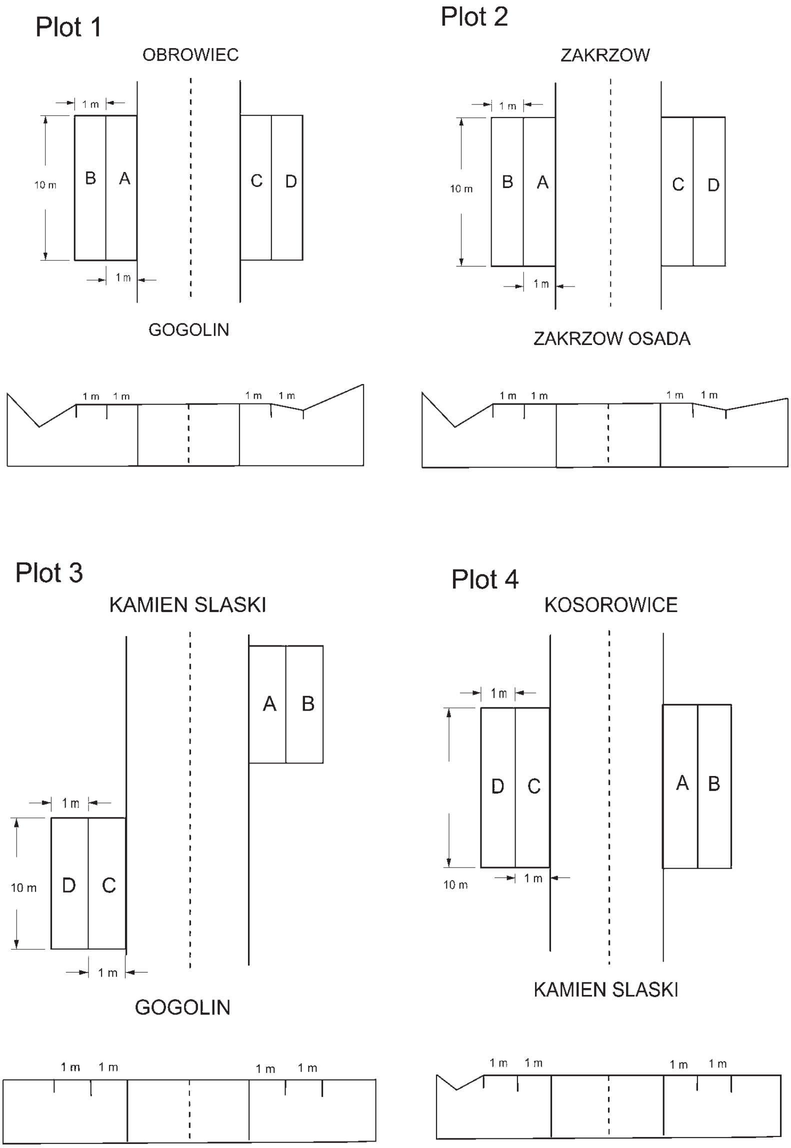

Fig. 1. Experimental plots located along roads

Table 1

The mechanical composition of roadside grounds

Zone of roadside	Percentage content of fractions with diameter [mm]												
	>2	<2	2–1	1–0.5	0.5–0.25	0.25–0.1	0.1–0.05	Σ **>0.05**	0.05–0.02	0.02–0.005	0.005–0.002	Σ **>0.002**	<0.002
1A	10	90	4	37	34	17	6	**98**	2	0	0	**2**	0
1B	12	88	5	19	34	23	5	**86**	4	0	8	**12**	2
1C	14	86	10	34	27	18	8	**97**	2	1	0	**3**	0
1D	18	82	3	25	32	19	14	**93**	6	0	0	**6**	1
2A	18	82	4	23	33	18	10	**88**	7	3	0	**10**	2
2B	9	91	5	16	24	15	16	**76**	14	6	0	**20**	4
2C	9	91	2	10	40	18	10	**80**	8	4	1	**13**	7
2D	9	91	5	17	30	18	0	**70**	18	5	0	**23**	7
3A	6	94	7	18	31	18	11	**85**	10	4	0	**14**	1
3B	7	93	6	19	30	22	9	**86**	8	4	0	**12**	2
3C	16	84	6	26	33	20	7	**92**	8	0	0	**8**	0
3D	10	90	2	21	27	20	14	**82**	7	6	0	**13**	3
4A	18	82	5	21	31	21	6	**79**	8	6	0	**14**	2
4B	18	82	8	24	29	19	7	**87**	9	2	0	**11**	2
4C	9	91	4	25	38	18	8	**93**	4	2	0	**6**	1
4D	6	94	3	25	38	19	5	**90**	7	1	0	**8**	2

the deep of 0–30 cm twice: in the autumn (November 2014) and spring (April 2015). Also control samples were taken in the distance of 4 meters from the road for every zone. The samples consist of 8 individual samples taken from each zone.

The samples were dried and then homogenized and then sieved. The samples were also divided into a few sections: elements bigger than 2 mm, elements sized 1.0–2.0 mm. In the section where elements were smaller than 1.0 mm aerometric Casagrand's method with Proszynski's modification was used to determine granulometric composition of the sample. The fractions bigger than 0.1 mm were determined granulometirically by using sieve and water method. The following chemical characteristics were also determined: saltiness by conductometric method based on electrolytic conductivity of water-soil mixture in weight proportion soil/water 1:5 and pH in H_2O and KCl by potentiometer (weight proportion soil/water 1 : 2,5).

Results and discussion

Granulometric composition. According to PTG criteria (2008) the analysis of the samples from test areas indicated that the soil is mainly built of sand (semiloam and loam) (Table 1). Only section 2D is an exeption – its soil has been classified as sandy loam. The presence of loose soil causes better water penetrability. That is why salt solution goes through the gaps in the soil quickly and causes smaller saltiness.

The pH values. Using the composition of coconut fibre and salt for eliminating slipperiness of the road did not change pH parameters negatively. The pH indicator of the samples showed neutral and minimal alkaline pH of soil. Before using the composite pH was about 6.36–7.03 and after applying the mixture it was about 6.60–7.23 (Fig. 2, 3). Many sources indicate that alkaline pH of soil can be caused by many factors both natural and anthropogenic. It is suggested that the pH increase after wintertime was caused by the features of the source rock. The samples were taken from the limestone background and it could cause higher pH in the spring. Findlay and Kelly states that increasing pH is caused by the change of ionic composition caused mainly by carbonate salts [11].

Analysis of the tests shows a specific link: the further the sample was from the road, the smaller the pH indicator. It can also be confirmed by other studies Chudecka et al [12].

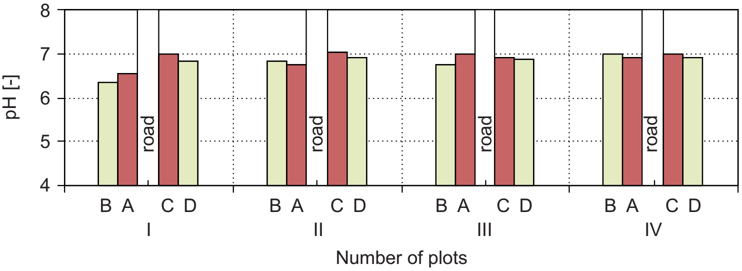

Fig. 2. The pH (1nKCl) values of roadside soil before applying the mixture of NaCl and coconut fibre (10:1) – autumn 2014

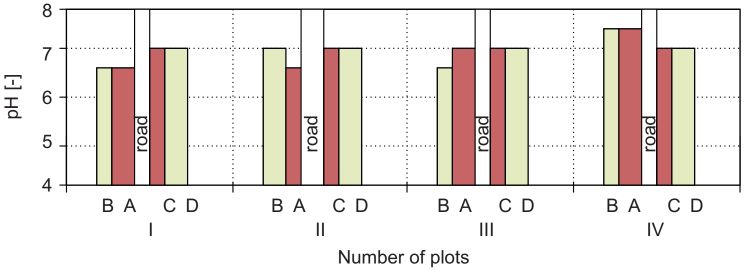

Fig. 3. The pH (1nKCl) values of roadside soil after applying the mixture of NaCl and coconut fibre (10:1) – spring 2015

Soil salinity. To determine the level of saltiness the key parameter is electrical conductivity. In the autumn the conductivity was about 190 μS · cm^{-1} and 50–160 μS · cm^{-1} in the spring. The smallest values were noticed in area number 1 and the biggest in area number 3 (Fig. 4, 5).

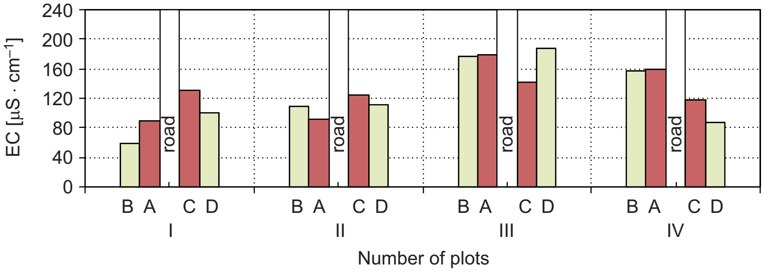

Fig. 4. Mean electrical conductivity (EC) of roadside soil before applying the mixture of NaCl and coconut fibre (10:1) – autumn 2014

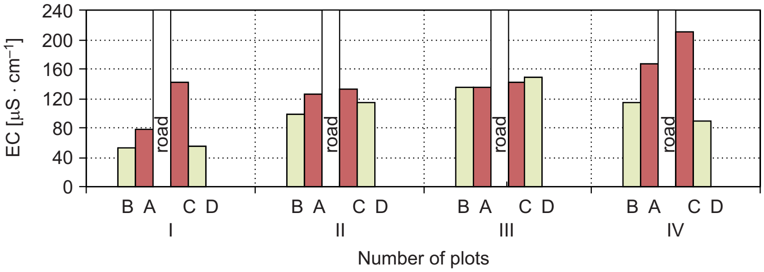

Fig. 5. Mean electrical conductivity (EC) of roadside soil after applying the mixture of NaCl and coconut fibre (10:1) – spring 2015

The results obtained during spring-autumn period indicated a decreasing tendency in electrical conductivity of soils collected from a ridge adjoining the roadway, from 140 to 125 μS · cm^{-1}. Whereas no difference was revealed in EC values in soils located in the distance of 1–2 m from the ridge road (Fig. 6) – mean EC value was 115 μS · cm^{-1}.

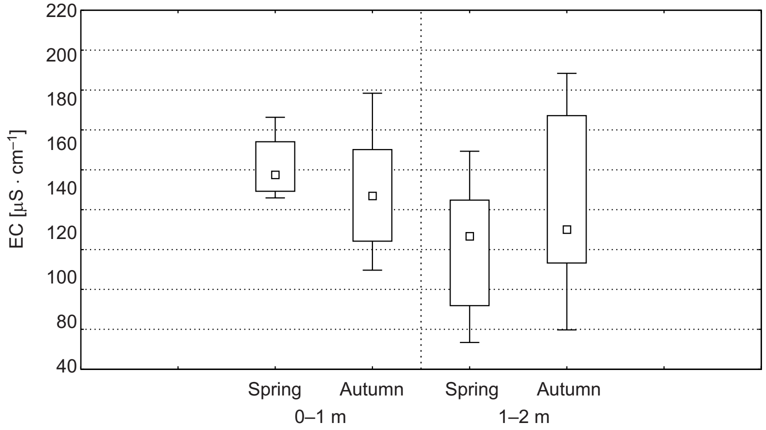

Fig. 6. Electrical conductivity values (EC) of roadside soil samples collected from experimental plots in autumn and spring

Significant deviation was observed in area I and III in the zones located the furthest from the road. The board value that indicates significant negative changes in soil is 2000 μS · cm^{-1}. The results do not exceed this value hence the soil is not heavily salted. After the study, the significant decrease of soil salinity was observed and the following dependence: the further the soil from the road, the smaller the conductivity. This relation is easily noticed for soil samples from area number 1, where the electrical conductivity indicator decreased by 15 % after applying the composite. Similar relations were confirmed by Brogowski's studies [13]. Small conductivity can be caused by the fact that easily dissolving salt from the mixture could sink into deep horizons of the ground [8, 14]. It can also be caused by using smaller amount of salt for eliminating the slipperiness on the road in this study than it is generally done. It can be stated that applying the mixture of salt and coconut fibre did not cause conductivity increase and it does not cause growth of soil salinity.

Conclusions

1. Using chemical substances in winter road maintaining causes deteriorating of roadside soil conditions. This is why there is a need for alternative ways of eliminating slipperiness which would affect natural environment less.

2. The test results based on soil samples from the chosen areas located next to roads indicated reduction of soil saltiness after applying the salt-coconut fibre composite. The results of the study are based on two conduciveness tests carried out in autumn and spring.

3. Using the salt-coconut fibre composite seems to be an alternative cheap way of eliminating slipperiness on roads. Quite long deposition of the mixture on the road caused gradual release of salt and by this, reduced the amount of used salt.

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WPŁYW KOMPOZYTU MIESZANKI WŁÓKIEN KOKOSOWYCH I SOLI STOSOWANYCH DO USUWANIA ŚLISKOŚCI JEZDNI NA GLEBY

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Abstrakt: Przedmiotem badań jest analiza wpływu zastosowanego kompozytu mieszanki włókna kokosowego i soli drogowej do usuwania śliskości drogowej na gleby w pasie przydrożnym. Badania laboratoryjne przeprowadzono na próbkach gleby pobranych z wyznaczonych poletek doświadczalnych w dwóch okresach: jesiennym przed zastosowaniem mieszanki oraz wiosną roku następnego. Analizy laboratoryjne wykazały głównie spadek wartości przewodnictwa właściwego po okresie zimowego stosowania zaproponowanego kompozytu, przyczyniając się do redukcji zasolenia gleb przydrożnych. Zastosowanie omawianej metody do usuwania śliskości jezdni może przyczynić się do zmniejszenia negatywnych skutków procesu zasolenia gleby w porównaniu z powszechnie stosowanymi technikami wykorzystującymi wyłącznie mieszanki samych soli.

Słowa kluczowe: zasolenie, usuwania śliskości drogowej, gleby przydrożne, włókna kokosowe, sole łatwo rozpuszczalne

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THE EFFECT OF MANGANESE TREATMENT ON PATHOGENIC FUNGI ISOLATED FROM BARLEY KERNELS

ODDZIAŁYWANIE NAWOZU MANGANOWEGO NA GRZYBY PATOGENICZNE IZOLOWANE Z ZIARNIAKÓW JĘCZMIENIA

Abstract: Teprosyn Mn manganese seed treatment, manufactured by a British firm Phosyn Chemicals Ltd., which was tested in the experiment, has been available on the Polish market for several years. Applied as a seed treatment it results in more intensive development of root system and improves general plant condition. However, in the available literature lacks information on Teprosyn Mn effect on plant healthiness or pathogenic organisms.

The aim of the paper was to compare the effect of Teprosyn Mn fertilizer and Raxil Gel 206 chemical seed treatment on pathogenic fungi species: *Fusarium culmorum* (W.G. Smith) Sacc., *Fusarium poae* (Peck) Wollen., *Fusarium avenaceum* (Fr.) Sacc., *Bipolaris sorokiniana* (Sacc. in Sorok.) Shoem. and *Botrytis cinerea* Pers.

In laboratory conditions the dynamics of growth and sporulation of the above mentioned fungi were assessed on PDA medium with a supplement of 0.1; 0.5 and 1.0 $mm^3 \cdot cm^{-3}$ of Teprosyn Mn and 0.005; 0.05 and 0.5 $mm^3 \cdot cm^{-3}$ of Raxil Gel 206. *In vitro* Teprosyn Mn manganese fertilizer reveals weak and diversified effect on linear growth of the studied phytopathogens. In the highest concentration (1.0 $mm^3 \cdot cm^{-3}$) it reduces the growth of *Fusarium avenaceum*, *Botrytis cinerea* and *Fusarium poae* colonies on the level of 7.3–10.1 %, whereas all its concentrations inhibit the sporulation process in *B. cinerea* i *F. avenaceum* from 35.3 % to 66 %. Along with increasing concentration in the medium its stimulating effect on linear growth of *Bipolaris sorokiniana* raises (5.7–18.3 %) and the spore number increases from 40 to 271.5 %.

Keywords: manganese treatment, pathogenic fungi, linear growth, sporulation

Introduction

Increasing the area under cereal crops greatly influences the species composition and harmfulness of numerous pathogens of these plants. On the other hand, among cereals,

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spring barley is the most infected by pathogenic fungi [1]. Obligatory pests, such as *Blumeria graminis* f. sp. *hordei* causing powdery mildew or *Puccina hordei* causing barley leaf rust are particularly oppressive on barley plantations [2–4] Also fungi transferred with the seeding material, such as *Bipolaris sorokiniana* or numerous *Fusarium* spp. species, which contribute to seedling blight or barley leaf spot, are also dangerous [5, 6]. In soil these organisms find convenient conditions for development, while a polyphagous character of *Fusarium* ssp. causes that they provide the main source of infection, also for numerous plant species. It has been estimated, that the losses of barley yield due to fungal diseases reach from 10 to 30 % [7, 8]. Chemical treatment of seed material is the most environment friendly, the most efficient and also the cheapest method of protection. Certified and carefully treated grain to a considerable extend guarantees reduction of diseases transferred with seed material and therefore obtaining better plant emergences leading to bigger yields [4, 9–12]. It is known from the literature reports that foliar macro and microelement fertilizers may also reduce the development of plant infectious diseases to a great extent [13–16]. On the other hand, *in vitro* they inhibit surface growth of phytopathogenic fungi [17, 18]. Teprosyn Mn manganese fertilizer, available on the market in Poland for several years, has been used as a seed treatment stimulating the development of cereal root system. The identification of the direct effect of this treatment on development of the pathogens colonizing barley kernels seems a necessary stage in the research on its influence on plant healthiness.

The paper aims to compare the effect of Teprosyn Mn seed treatment and Raxil Gel 206 chemical treatment on *Fusarium culmorum* (W.G. Smith) Sacc., *Fusarium poae* (Peck) Wollen., *Fusarium avenaceum* (Fr.) Sacc., *Bipolaris sorokiniana* (Sacc. in Sorok.) Shoem. and *Botrytis cinerea* Pers pathogenic fungi colonizing seeds of spring barley, ‘Poldek’ c.v.

Materials and methods

Pathogenic fungi*: Fusarium culmorum* (W.G. Smith) Sacc., *Fusarium poae* (Peck) Wollenw., *Fusarium avenaceum* (Fr.) Sacc., *Bipolaris sorokiniana* (Sacc.) Shoemaker and *Botrytis cinerea* Pers, most frequently isolated from malting barley, ‘Poldek’ c.v., were selected for the laboratory experiment which was conducted in 2012. Teprosyn Mn seed treatment with guaranteed 27.4 % content of total manganese and chemical treatment Raxil Gel 206 with active substances: tiuram – 200 g and tebukonazol – 6 g per 1 dm^3 of the substance, was used in the experiment.

Seed treatments were added to the PDA medium in the amounts allowing to obtain their concentrations, respectively for Teprosyn Mn 0.1; 0.5 and 1.0 $mm^3 \cdot cm^{-3}$ and for Raxil Gel 206: 0.005; 0.05 and 0.5 $mm^3 \cdot cm^{-3}$. Prepared media were inoculated with an agar disc, 5 mm in diameter, overgrown with three-week old mycelium of the analysed organism. The control was provided by Petri dishes with clean PDA medium. The test fungi were cultured *in vitro* in five replications for each combination. The assessment of sporulation was conducted on 20-day old fungi cultures. A drop of spore suspension was placed in Thom hemocytometer under the light microscope and the spore number was counted.

The effect of individual seed treatment and its concentration on linear growth and sporulation of the analysed fungi was expressed as linear growth/sporulation inhibition index according to Abbot formula [19]:

$$I = \frac{K - A}{K} \cdot 100 \ \%$$

where: I – index of fungi linear growth/sporulation inhibition,
K – mean diameter of fungi colony on a plate/number of control spores,
A – mean diameter of colony/number of fungi spores in individual test object.

Moreover, the coefficient of linear growth rate was computed on the basis of daily measurements of fungi surface growth in each combination [14]:

$$T = \frac{A}{D} + \frac{b_1}{d_1} + \ldots + \frac{b_x}{d_x}$$

where: T – linear growth rate,
A – diameter from diameter measurements,
D – number of days from the experiment outset,
b_1, b_2 – increment of colony diameter since the last measurement [mm],
d_1, d_2 – number of days since the last measurement.

The results were subjected to the analysis of variance and the significance of differences was verified by t-Student test on the significance level $\alpha = 0.05$.

Results and discussion

The experiments confirmed a high fungistatic activity of Raxil Gel 206 chemical seed treatment, which was the point of reference for an assessment of Teprosyn Mn seed treatment effect on fungal organisms. In the first place the treatment guarantees a better development and linear growth of cereal crops. The phytopathogenic fungi analyzed *in vitro* responded to Teprosyn Mn treatment supplement to the medium quite variably (Table 1).

Table 1

Effect of seed treatments on the tested fungi linear growth rate

Type of preparation	Tested fungi linear growth rate, T				
	Fusarium avenaceum	*Fusarium culmorum*	*Fusarium poae*	*Botrytis cinerea*	*Bipolaris sorokiniana*
Raxil Gel 206	8.41	3.09	4.68	10.10	9.36
Teprosyn Mn	73.92	81.39	83.01	70.82	65.12
Control	72.34	77.12	88. 49	73.65	62.79
$LSD_{0.05}$	1.86	5.44	2.81	4.08	4.88

Irrespective of the applied concentration, the treatment stimulated surface growth of *Fusarium avanaceum*, *Fusarium poae* and *Bipolaris sorokiniana* mycelium, however, no significant differences in the values of linear growth coefficients were registered in comparison with the control. Moreover, despite small reduction observed in *Botrytis cinerea* fungus growth rate on the medium with added Teprosyn Mn, statistical analysis did not reveal any significant differences in comparison with the control. Only in case of *Fusarium poae,* the preparation markedly limited the rate of its colony surface growth. On the other hand, Raxil Gel 206 chemical treatment very strongly inhibited growth of all tested fungi, as evidenced by very low values of the linear growth rate coefficients.

In the presented experiments the kind of seed treatment modified not only the surface growth of the tested phytopathogen colonies, but also their concentration in the medium (Table 2). Moreover, individual fungi revealed different sensitivity to the applied preparations and their concentrations. Obtained results prove a lack of fungistatic effect of the analysed concentrations of Teprosyn Mn on *B. sorokiniana*.

Table 2

Linear growth rate coefficient, *T*, of tested fungi depending on the kind and concentration of seed treatments

Type of preparation	Concentration [$mm^3 \cdot cm^{-3}$]	*Fusarium avenaceum*	*Fusarium culmorum*	*Fusarium poae*	*Botrytis cinerea*	*Bipolaris sorokiniana*
Teprosyn Mn	1.0	66.44 c*	80.24 b	80.12 c	66.63 c	68.42 c
	0.5	76.16 e	79.24 b	82.39 cd	73.00 c	65.99 c
	0.1	79.15 e	84.69 b	86.54 de	72.83 c	62.95 c
Raxil Gel 206	0.5	2.76 a	1.00 a	0.60 a	5.52 a	5.72 a
	0.05	5.57 a	3.73 a	1.79 a	11.40 ab	8.12 ab
	0.005	16.89 b	4.55 a	11.65 b	13.38 b	14.25 b
Control		72.34 d	77.12 b	88.49 e	73.65 c	62.79 c

* Values in columns marked by the same letter are not significantly different.

A comparison of coefficients of the rate and inhibition of linear growth shows that *B. sorokoniana* species was the most resistant both to Raxil Gel 206 and Teprosyn Mn (Tables 2 and 3).

Table 3

Coefficients of inhibition/stimulation, *I,* of tested fungi linear growth

Type of preparation	Concentration [$mm^3 \cdot cm^{-3}$]	*Fusarium avenaceum*	*Fusarium culmorum*	*Fusarium poae*	*Botrytis cinerea*	*Bipolaris sorokiniana*
Teprosyn Mn	1.0	7.28	+5.66	10.09	8.16	+18.29
	0.5	+4.46	+3.43	7.76	2.92	+16.77
	0.1	+8.45	3.88	3.33	+6.12	+5.70
Raxil Gel 206	0.5	90.38	95.86	95.73	86.91	83.51
	0.05	86.62	90.42	93.20	79.36	79.78
	0.005	73.44	89.11	82.33	76.19	69.52

On media with Raxil Gel 206 chemical treatment supplement linear growth was inhibited starting from the lowest concentration in the range from 69.52 % to 83.51 % (Table 3). On the other hand, the manganese fertilizer concentrations of 1.0 and 0.5 $mm^3 \cdot cm^{-3}$ caused stimulation of *B.sorokiniana* colony growth by 18.29 % and 16.77 %, respectively.

Fusarium species more strongly responded to the presence of tested preparations in the medium. However, among them *F. poae* proved the most sensitive, as its strong inhibition was noted on the media containing Raxil Gel 206. All concentrations (0.5, 0.05 and 0.005 $mm^3 \cdot cm^{-3}$) inhibited its colony linear growth within the range of 95.73–82.33 % (Tables 2 and 3). Similarly, with increasing concentration of Teprosyn in the medium a stronger inhibition of *F. poae* hyphae growth was registered. It is worth emphasizing that for the same pathogen Teprosyn Mn revealed an opposite effect than on *B. sorokiniana*. Higher concentrations 1.0 and 0.5 $mm^3 \cdot cm^{-3}$ of the manganese treatment stimulated the growth of *F. culmorum* mycelium only to a small extend (5.66–3.43 %) (Table 3). The preparation concentrations of 0.5 and 0.1 $mm^3 \cdot cm^{-3}$ contributed to a faster growth of *F. avenaceum* colony, whereas the lowest concentration favoured also *B. cinerea* fungi growth (Table 3). On the other hand, weak limiting effect on surface growth of *B. cinerea* colony was observed on media containing higher concentrations (1.0 and 0.5 $mm^3 \cdot cm^{-3}$) of Teprosyn Mn treatment. Only 7.0 % inhibition of *F. avenaceum* colony linear growth was registered in the combination with 1.0 $mm^3 \cdot cm^{-3}$ (Teprosyn Mn dose recommended for seed treatment) (Table 3).

Authors' own investigations revealed that the tested preparations and their concentrations more strongly affected sporulation in the tested fungi than the surface growth of hyphae. Spores produced by fungi existing on seeds play a crucial role in the pathogenesis process, since they are responsible for plant infection which is the first stage of disease process. Moreover its endospores allow to survive under unfavourable environmental conditions [20–22]. Therefore, pathogenic fungi which have no conditions for developing hyphae start to product a greater number of spores and these in turn ensure viability and the continuity of the species [23].

The strongest stimulating effect of manganese treatment on linear growth of *B. sorokiniana* was reflected in its sporulation process. In combination with the highest concentration of Teprosyn Mn, the registered number of spores was 271 % bigger than in the control and was diminishing successively to 129 % and 46 % along with decreasing concentration of the preparation in the medium. On the other hand, on media containing 1.0 $mm^3 \cdot cm^{-3}$ of Teprosyn Mn treatment an increase in macroconidia number was observed in *F. poae* by 75.75 % and in *F. culmorum* by 53.11 % (Fig. 1), whereas a relatively strong inhibition of sporulation, between 61 and 66 % was noted in *F. avenaceum* and slightly lower (35–61 %) for *B. cinerea*.

With few exceptions, Raxil Gel 206 seed treatment strongly inhibited sporulation process in the tested fungal organisms (Fig. 2). The preparation in concentrations of 0.5 and 0.05 $mm^3 \cdot cm^{-3}$ almost totally blocked spore production by *B. sorokiniana* fungus.

It should be noticed that the linear growth tests revealed the weakest fungistatic effect of Raxil Gel 206 on this pathogen (Table 3).

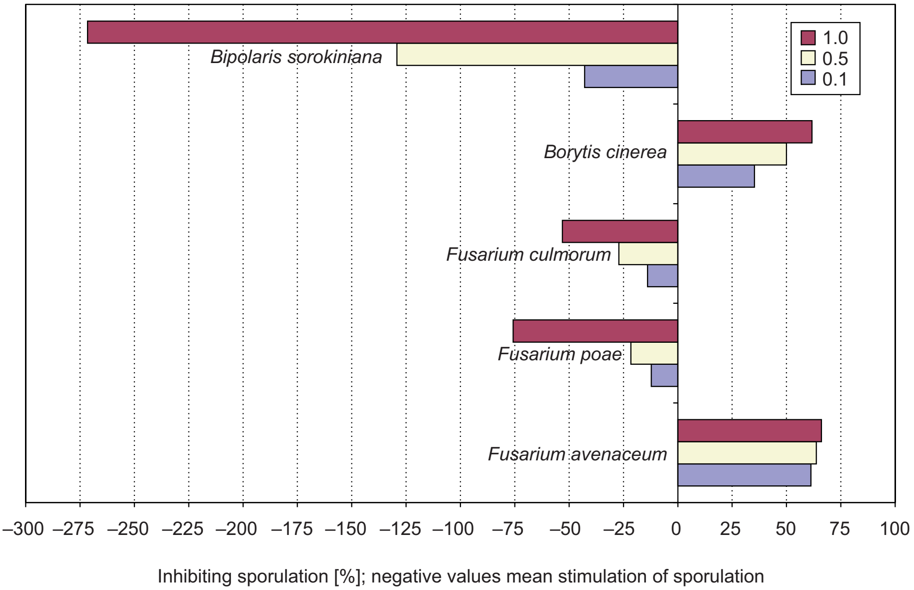

Fig. 1. Effect of Teprosyn Mn treatment on test fungi sporulation

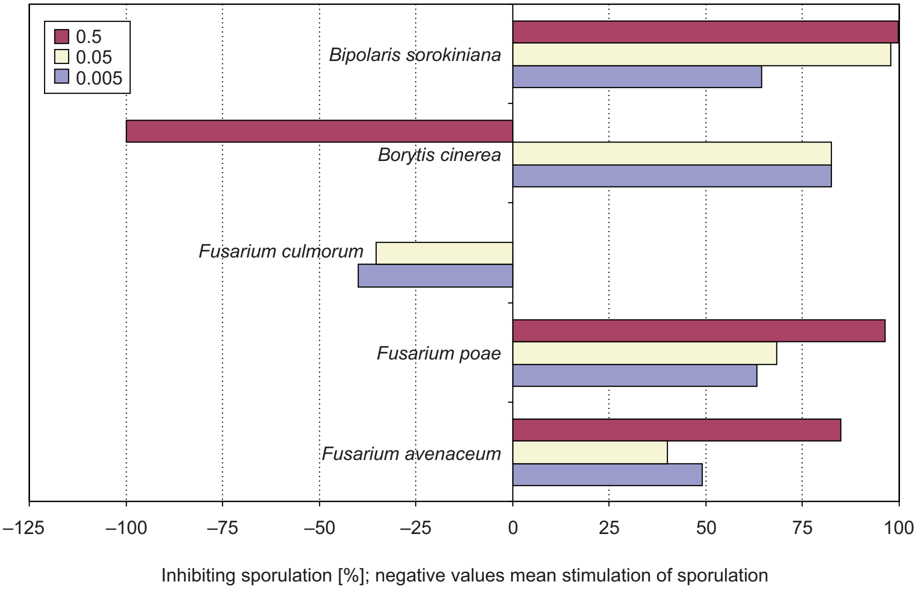

Fig. 2. Effect of Raxil Gel 206 seed treatment on the test fungi sporulation

Very strong inhibition of *F. poae* sporulation, reaching 96.30 %, was also registered on the medium with 0.5 $mm^3 \cdot cm^{-3}$ of this seed treatment (Fig. 2). In the conducted experiments Raxil Gel 206 revealed quite changeable effect on sporulation process in

B. cinerea and *F. culmorum*. In case of the first species, on the media containing 0.05 and 0.005 $mm^3 \cdot cm^{-3}$ of this preparation the number of spores was by 82.35 % lower than on the control, whereas for *F. culmorum* it was bigger by 35 and 40 %, respectively. On the other hand, on the medium with the highest concentration of Raxil Gel 206 a strong stimulation (100 %) of *B. cinerea* fungus sporulation was observed (Fig. 2). Intensified spore production by fungi mentioned above confirms the Hodges' rule [25], *ie* at confirmed strong inhibition of *F. culmorum* and *B. cinerea* surface growth on the medium with 0.5 $mm^3 \cdot cm^{-3}$ of Raxil gel 206 (Fig. 2) scarce fungi hyphae were producing a greater number of spores. The phenomenon should be treated as a defence mechanism of these fungal organisms against the unfavourable environmental conditions. In the light of conducted research, Teprosyn Mn seed treatment may in agricultural practice reveal poor protective properties of cereal grain against such fungi as *F. avenaceum* and *B. cinerea*.

Conclusions

1. Raxil Gel 206 used for *in vitro* tests very strongly inhibited surface growth of the tested fungi, irrespective of the applied concentration, whereas in 0.5 $mm^3 \cdot cm^{-3}$ concentration almost totally blocked sporulation process in *B. sorokiniana* (99.7 %) and *F. poae* (96.3 %) and in 100 % stimulated spore production by *B. cinerea*.
2. Teprosyn Mn manganese treatment in laboratory conditions revealed weak and diverse effect on linear growth of tested phytopathogens. Its highest concentration (1.0 $mm^3 \cdot cm^{-3}$) limited *F. avenaceum*, *B. cinerea* and *F. poae* colony growth by between 7.3 and 11.0 %.
3. All concentrations of Teprosyn Mn inhibited sporulation process in *B. cinerea* and *F. avenaceum* by between 35.3 and 66 %. With growing concentration in the medium its stimulating effect on *B. sorokiniana* linear growth increased (5.7–18.3 %) and the spore number grew from 40 to 217.5 %.

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ODDZIAŁYWANIE NAWOZU MANGANOWEGO NA GRZYBY PATOGENICZNE IZOLOWANE Z ZIARNIAKÓW JĘCZMIENIA

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Abstrakt: W doświadczeniu testowano nawóz manganowy Teprosyn Mn, produkowany przez angielską firmę Phosyn Chemicals Ltd., który od kilku lat jest on dostępny na polskim rynku. Efektem jego stosowany jako zaprawy nasiennej (nawóz donasienny) jest intensywniejszy rozwój systemu korzeniowego oraz polepszenie ogólnej kondycji roślin. W dostępnej literaturze brakuje informacji dotyczących oddziaływania Teprosynu Mn na zdrowotność roślin oraz organizmy patogeniczne.

Celem pracy było porównanie oddziaływania nawozu donasiennego Teprosyn Mn i chemicznej zaprawy nasiennej Raxil Gel 206 na patogeniczne gatunki grzybów: *Fusarium culmorum* (W.G. Smith) Sacc., *Fusarium poae* (Peck) Wollen., *Fusarium avenaceum* (Fr.) Sacc., *Bipolaris sorokiniana* (Sacc. in Sorok.) Shoem. i *Botrytis cinerea* Pers.

W warunkach laboratoryjnych oceniono dynamikę wzrostu i sporulację wymienionych grzybów na podłożu (PDA) z udziałem 0.1; 0.5; 1.0 $mm^3 \cdot cm^{-3}$ Teprosynu Mn oraz 0.005; 0.05; 0.5 $mm^3 \cdot cm^{-3}$ Raxil Gel 206. Nawóz manganowy Teprosyn Mn w warunkach *in vitro* wykazuje słabe i zróżnicowane oddziaływanie na rozrost liniowy badanych fitopatogenów. W największym stężeniu (1.0 $mm^3 \cdot cm^{-3}$) ogranicza o 7,3 do 10,1 % rozrost kolonii: *Fusarium avenaceum*, *Botrytis cinerea* i *Fusarium poae*. Natomiast we wszystkich stężeniach hamuje proces wytwarzania zarodników przez *B. cinerea* i *F. avenaceum* w zakresie od 35,3 % do 66 %. Wraz ze zwiększaniem stężenia w podłożu hodowlanym rośnie jego stymulujące oddziaływanie na wzrost liniowy *Bipolaris sorokiniana* (od 5,7 do 18,3 %) oraz zwiększa się ilość zarodników od 40 do 271,5 %.

Słowa kluczowe: nawóz manganowy, grzyby fitopatogenne, wzrost liniowy, zarodnikowanie

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USING ASH FROM INCINERATION OF MUNICIPAL SEWAGE SLUDGE TO FERTILIZE VIRGINIA FANPETALS

WYKORZYSTANIE POPIOŁÓW ZE SPALANIA KOMUNALNYCH OSADÓW ŚCIEKOWYCH DO NAWOŻENIA ŚLAZOWCA PENSYLWAŃSKIEGO

Abstract: The purpose of this paper was to determine the effect of ash from a sewage sludge incinerating facility on yields and mineral composition of Virginia fanpetals, and on the content of heavy metals in soil. The study was based on a pot experiment in which ash obtained from sewage sludge incineration at the Lyna Wastewater Treatment Plant was used as a substitute of mineral fertilizers. The dominant fertilizing ingredients found in the analyzed ash were phosphorus and calcium. The content of cadmium and lead was lower than the allowable concentrations of these metals in mineral fertilizers. Ash from incinerated sewage sludge did not have any substantial effect on the soil content of the mobile forms of cadmium, copper, lead and chromium. With respect to three metals, namely nickel, zinc and manganese, the medium and high doses of ash raised significantly their concentrations in soil. The rate of ash had no influence on the content of sodium and magnesium in the plants but when the highest dose of ash had been applied, the concentration of calcium in plants rose significantly. Ash modified the content of heavy metals in the plant material only very slightly.

Keywords: ash from incineration of municipal sewage sludge, Virginia fanpetals, phosphorus, heavy metals, soil

Introduction

Diminishing resources of fossil fuels as well as the threat of climate change due to excessive emission of carbon dioxide force people to search for sources of renewable energy. Among the possibilities tested it plant biomass.

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Solid biomass is obtained from waste by-products derived from forestry, agriculture, the timber industry and urban greenery care; some small quantities are also acquired from sorted municipal organic waste. Today, the biomass supply on the energy market can be enriched with biomass produced on field plantations of perennial energy crops [1]. Virginia fanpetals, also known as Virginia mallows (*Sida hermaphrodita*) is such energy crop, grown for its large yields of stems and leaves and known for durable plantations. This plant is also recommended for phytoremediation and rehabilitation of chemically polluted soil because when grown on substrate with an elevated content of heavy metals, it produces quite good yields and accumulates substantial amounts of heavy metals [2].

In 2011, a total of 519. million Mg d.m. of sewage sludge was generated, of which 8 % (41.6 million Mg d.m.) was processed thermally. The waste management plan for 2014 in Poland presumes further reduction of the amount of stored sludge and an increase in the quantity of municipal sewage sludge processed, including high temperature processing (about 30 %), prior to reintroduction to the environment [3]. Also, it is emphasized that the extent of utilization of biogenic substances found in sludge should be maximized, yet the requirements set to ensure sanitary and chemical safety must be met.

Incineration of sewage sludge reduces considerably the volume of such waste. Numerous studies have also implied that ash from combustion of sewage sludge can be used as active ingredient replacing some part of cement, but specific requirements must be met before sewage sludge ash is used in building practice [4–7]. Ash contains high quantities of phosphorus compounds and is therefore valuable raw product for manufacture of fertilizers [8–10] or baked pellets used for wastewater treatment in hydrophyte systems [11]. Two other essential nutrients found in sewage sludge ash are calcium and magnesium, while potassium and sodium are present in smaller amounts. The content of phosphorus in ash from incineration of municipal sewage sludge can be up to 260 $gP_2O_5 \cdot kg^{-1}$ d.m. and is therefore comparable to its concentration in poor quality phosphates [6]. Such ash can also be used for production of technical phosphoric acid [12].

The purpose of this paper has been to evaluate the influence of ash from a sewage sludge incineration facility on yields and mineral composition of Virginia fanpetals and on the soil content of heavy metals.

Material and methods

A two-year of one-factor experiment with four replications was conducted in a greenhouse, at the University of Warmia and Mazury in Olsztyn. Kick-Brauckmann pots were filled with 10 kg of substrate of the grain size distribution of light loamy sand. The substrate was characterized by slightly acid reaction (pH_{KCl} = 5.6), moderate availability of accessible phosphorus (63.2 $mgP \cdot kg^{-1}$), high availability of potassium (125.5 $mgK \cdot kg^{-1}$) and moderate availability of magnesium (62.0 $mgMg \cdot kg^{-1}$). Nitrogen and potassium were applied in the form of mineral fertilizers (ammonium nitrate and potassium chloride), and the source of phosphorus added to soil was ash from incineration of sewage sludge originating from the Lyna WTP in Olsztyn (Table 1). Rates of ash were determined according to its concentrations of phosphorus (Table 2). Virginia fanpetals plant were cultivated from root cuttings. The control treatment was composed of plants grown without fertilization.

Table 1

Design of experiment

Treatment	Fertilization [g per pot]		
	N	P	K
Control	0.0	0.00	0.0
P1	0.5	0.25	0.5
P2	1.0	0.50	1.0
P3	1.5	0.75	1.5

After harvest, plants were weighed and dried. Following digestion in concentrated sulphuric acid(VI) with hydrogen dioxide as oxidizing agent, plant material was submitted to determination of concentrations of the following elements (determination methods in brackets): nitrogen (by colorimetry with the hypochlorite method), phosphorus (by colorimetry with the vanadium-molybdene method), potassium, calcium and sodium (by atomic emission spectrophotometry) and magnesium (by atomic absorption spectrophotometry). The content of heavy metals was determined by the AAS method, having previously mineralized plant material in a mixture of nitric acid(V) and chloric acid(VII) (in a 4:1 ratio) with added hydrochloric acid.

Determinations of the content of mobile forms of heavy metals before the experiment and after the harvest were performed with the AAS method, after extraction in 1 mol HCl dm^{-3}.

Easily soluble forms of heavy metals were extracted from ash in 1 mol HCl $\cdot$ dm^{-3} while hardly soluble ones were hot extracted in concentrated sulphuric acid.

The results of chemical determinations were submitted to statistical analysis aided by Statistica 10 software package. All statistical calculations were performed at the level of significance $p = 0.01$. Fisher's test was applied to verify the significance of differences.

Results and discussion

The results of our examination of the fertilizing properties of ash from the municipal sewage sludge incineration facility at the Lyna Wastewater Treatment Plant in Olsztyn (Table 2) were congruent with relevant data found in literature [6, 11–15] regarding the alkaline nature of ashes, high concentration of phosphorus (62.48 gP $\cdot$ kg^{-1} d.m.) and alkaline metals (44.09 gCa $\cdot$ kg^{-1} d.m. and 12.30 gMg $\cdot$ kg^{-1} d.m.). Same as in the experiments of Bialowiec et al [11] and Ciesielczuk et al [13], other fertilizing elements such as carbon and nitrogen appeared in small quantities.

Table 2

Fertilization properties of ash from incineration of sewage sludge

Dry matter content [%]	pH_{H_2O}	$C_{org.}$ [%]	N	P	Ca	Mg	Na
			[g · kg^{-1} d.m.]				
88.45	8.28 ± 0.07	3.14 ± 0.33	2.19 ± 0.06	62.48 ± 1.27	44.09 ± 4.41	12.30 ± 1.59	14.03 ± 1.28

The X-ray diffraction of ash from sewage sludge burning showed that the high temperature reaction of iron phosphate with the calcium compounds present in sewage sludge generates mixed calcium and iron phosphate ($Ca_9Fe(PO_4)_7$) and hematite [16]. These compounds greatly condition the potential leaching of phosphorus from ash. Owing to their presence, the availability of the forms of phosphorus soluble in citric acid may be as high as 50 % of the total content of this element in ash. Some other research [17] demonstrated that the availability of phosphorus in ash obtained from incineration of a mixture of meat and bone meal (MBM) and sewage sludge (in a 3 to 1 ratio) is as high as 65 % because no presence of hydroxyapatite or tricalcium phosphate ($Ca_3(PO_4)_2$) was detected during the calcination process. These two compounds are most probably decomposed by reacting with iron phosphate present in sewage sludge.

In our examinations, we determined the content of easily soluble (extraction in 1 mol HCl · dm^{-3}) and hardly soluble (extraction in concentrated H_2SO_4) forms of heavy metals (Table 3). Zinc appeared in the highest amount, followed by manganese and copper. The share of the hardly soluble form of heavy metals, with respect to the easily soluble one, ranged from 7 % (chromium) to 62 % (manganese). Latosinska and Gawdzik [18] indicated that heavy metals in sewage sludge ash were dominant in immobile fractions. These metals were bound with alumosilicates, sulfates and permanent organometalic connections. The allowable concentrations of some heavy metals in commercially available mineral fertilizers (arsenic, cadmium, lead and mercury) are defined in The Introduction of Fertilizers on the Commercial Market. Among the metals analyzed in the tested ash, cadmium and lead appeared in the quantities below the allowable limits.

Table 3

Content of heavy metals in ash from incinerated sewage sludge

Specification	Cd*	Cu	Pb**	Ni	Cr	Zn	Mn
	[mg · kg^{-1} d.m.]						
Easily soluble	0.66	396.2	33.16	9.54	10.14	789.0	625.0
Hardly soluble	1.12	870.6	70.09	49.36	128.81	3181.4	1102.4
Share of easily soluble form [%]	50	45	47	19	7	24	62

* Allowable content in mineral fertilizers 50 mgCd · kg^{-1} d.m.; ** allowable content in mineral fertilizers 140 mgPb · kg^{-1} d.m. [19].

Bialowiec et al [11] demonstrated low leachability of contaminants from ash originating from incinerated sewage sludge. Aqueous extracts were characterized by high pH, which may prove high immobilization of heavy metals and translates to their almost negligible leaching.

Fu-Shen Zhang et al [20] demonstrated that alkalinity (calcification effect) of ashes from organic waste corresponds to 10–30 % CaO and is particularly high in ashes from incinerated sewage sludge [13]. The content of plant available phosphorus relative to the total concentration of this element was about 37.6 % (27–44.5 %). The content of calcium in ash was 3- to 12-fold higher than in soil, while that of potassium exceeded the coil concentration by 1.3–6-fold. The concentrations of heavy metals (Ni, Cu, Zn, Cd, Sn, Pb) in ash generated by incinerating sewage sludge was 10- to 200-fold higher than their levels in soils in Japan [20].

Ash from incineration of sewage sludge is a prospective source of phosphorus for making phosphate fertilizers. Due to its high content of heavy metals and a relatively low bioavailability of phosphorus, prior to being used in farming, sewage sludge ash must be detoxicated with thermochemical methods. Increasing the availability of phosphorus to plants through acid processing has been described by several authors [21–23].

Phosphates recovered from sewage sludge ashes produce good fertilizing output without having adverse effects on plants. Considering the fact that agricultural use of raw sewage sludge will most definitely continue to decrease (in Switzerland it is even prohibited), phosphorus recycling will become indispensable. Treatment of ashes from sewage sludge incineration creates a more rational waste management option, as it is both friendly to the environment and focuses on identification and recycling of valuable ingredients [9]. However, due to a relatively high load of heavy metals (especially Cd, Cr, Cu, Ni, Pb and Zn), before being used in farming sewage sludge ash must be treated chemically or physically in order to decrease its content of the above contaminants below the legally binding maximum limits [8].

According to Kalmykova and Karlfeldt Fedje [24], amounts of phosphorus generated every year and arrested in the residues left after incineration of solid municipal waste could cover up to 30 % of the annual demand for phosphorus fertilizers in Sweden. The concentration of phosphorus in ash is slightly higher than in sewage sludge but the substance is not allowed to be applied on arable lands in that country because of its content of heavy metals. However, it would be beneficial to use it as a raw resource for production of fertilizers instead of phosphates.

A study by Ciesielczuk et al [13] revealed high differentiation in the content of heavy metals in ash from incinerated plant biomass. These authors found particularly high amounts of manganese, zinc and copper, which might be a factor justifying the use of ash as a source of supply of these elements to plants. In the light of the current legal regulations, due to the content of lead in excess of the set norm, ash from incineration of pine timber should be excluded from agricultural use.

The soil taken for our experiment was characterized by natural levels of heavy metals (Table 4). Ash applied to fertilize Virginia fanpetals elevated these concentrations but without exceeding the norms set for unpolluted soils. In respect of nickel, zinc and manganese, their concentrations in soil increased in proportion to the rate of ash. The highest ash dose, compared to the control, doubled the soil content of nickel forms soluble in 1 mol dm^{-3} HCl. As for the other heavy metals, the observed changes were much smaller and frequently appeared incidental.

Table 4

Content of heavy metals in soil

Rate of ash	Cd	Cu	Pb	Ni	Cr	Zn	Mn
	$[\mathrm{mg \cdot kg^{-1}\ d.m.}]$						
	Before the experiment						
	0.05 ± 0.02	1.48 ± 0.14	3.38 ± 0.57	1.76 ± 0.49	0.55 ± 0.13	9.48 ± 0.95	70 ± 19
	After harvest						
Control	0.053a*	2.360a	4.117a	0.806a	0.806a	11.50a	80.10b
P1	0.083a	2.321a	5.685a	1.186ab	0.779a	12.10a	76.49ab
P2	0.029a	2.190a	5.329a	1.265ab	0.757a	14.24b	87.27a
P3	0.044a	2.194a	5.018a	1.604b	0.751a	14.68b	88.89a

* Data designated with same letters do not differ significantly at $P \leq 0.01$.

Bielinska et al [25] did not determine any significant increase in soil concentrations of Zn, Cu or Cd in light soil enriched with fluidized ashes from hard coal in a rate calculated according to their content of CaO and the soil's liming demand. Other authors as well suggested that properly modified fluidized ashes can be used to improve the properties of soil [26]. Fu-Shen Zhang et al [20] concluded that sewage sludge ashes can be used to de-acidify acid soils. However, due to their content of heavy metals and the permissible maximum levels of copper in soil (125 mgCu · kg^{-1}), the amount of ash which can be introduced to soil is 40–80 Mg · ha^{-1}. The cited researchers emphasize that it would be recommendable to subject ashes to preliminary removal of heavy metals before they are introduced to soil.

Kovacik et al [27] noticed that in response to ashes (in doses from 3 to 150 Mg · ha^{-1}) added to soil together with NPK fertilizers, the soil's pH increased and the amounts of plant available calcium, magnesium and potassium as well as the content of total carbon were higher. At the same time, the cation exchange capacity (CEC), total exchangeable bases (TEB) and base saturation (BS) increased whereas the bulk density of soil went down. The disadvantageous effect of the application of ashes was the decreasing content of total nitrogen and higher salinity of soil.

The fertilization level and associated rates of sewage sludge ash had a weak effect on the content of heavy metals in Virginia fanpetals plants, and the observed changes were inconsistent (Table 5). In an experiment by Borkowska and Lipinski [28], intensive nitrogen fertilization significantly decreased the concentration of nickel but a higher dose of phosphorus fertilizer contributed to a decreased amount of nickel in biomass of Virginia fanpetals.

Table 5

Content and uptake of heavy metals by Virginia fanpetals

Rate of ash	Cd	Cu	Ni	Cr	Zn	Mn
	$[mg \cdot kg^{-1}$ d.m]					
Control	0.25a*	2.17a	21.26a	1.62a	19.94a	69.29a
P1	0.40c	2.25a	21.57a	8.03b	28.38a	131.98a
P2	0.21a	2.11a	21.08a	8.81b	19.29a	77.60a
P3	0.35b	2.19a	19.28a	2.10a	22.89a	119.62a
Uptake [mg per pot]						
Control	0.005	0.046	0.455	0.035	0.426	1.482
P1	0.013	0.076	0.726	0.270	0.955	4.440
P2	0.011	0.110	1.099	0.459	1.006	4.046
P3	0.020	0.123	1.081	0.118	1.284	6.710

* Data designated with same letters do not differ significantly at $P \le 0.01$.

Nitrogen and phosphorus contents in the aboveground mass of Virginia fanpetals increased proportionally to the dose of the ash (Table 6). The plants after the application of the average dose of ash had indeed highest N concentration, while the highest levels of P (2.36 times more than in control plants) was found in plants fertilized with the highest ash dose. The concentration of potassium and magnesium in the control plants was similar to the quantities of these components in Virginia fanpetals fertilized with the highest dose of ash. A significant increase of the calcium content in plant material was found only after the application of the highest dose of ash.

Table 6

Content of macronutrients in Virginia fanpetals

Dose of ash	N	P	K	Na	Mg	Ca
	$[g \cdot kg^{-1}$ d.m.]					
Control	6.15a*	1.65a	37.00b	0.05a	2.24a	27.22a
P1	6.21ab	1.72a	28.75a	0.22b	1.77ab	26.72a
P2	8.50b	1.58a	29.90a	0.25b	1.73b	27.76a
P3	7.47ab	3.89b	34.98b	0.21b	2.39a	33.08b

* Data designated with same letters do not differ significantly at $P \le 0.01$.

Intensive nitrogen and phosphorus fertilization did not affect significantly the content of macronutrients and chlorine in Virginia fanpetals. Nourishment with potassium in the form of sulphide, compared to chloride, depressed the content of nitrogen, magnesium, calcium and chlorine in Virginia fanpetals [29] No significant changes in the content of crude ash or macronutrients caused by different rates of phosphorus fertilizers were observed [26]. Kalembasa [30] reported that incineration of Virginia fanpetals biomass generates 59.5 $kg \cdot Mg^{-1}$ of crude ash, and the amount of pure ash is 16.0 $kg \cdot Mg^{-1}$.

The high crude to pure ash ratio (3.72) implicates high concentrations of silicate and carbonates. The dominant elements were calcium (66.3 %) and potassium (11.0 %), while zinc (0.10 %) was the prevailing heavy metal. Antonkiewicz [31] conducted an experiment on use of sewage sludge for rehabilitation of furnace ash disposal sites and found the highest content of Mg, Ca and K in a mix of grasses with white clover nourished with furnace ash alone, while the content of P and Na was the highest in plants fertilized with just sewage sludge.

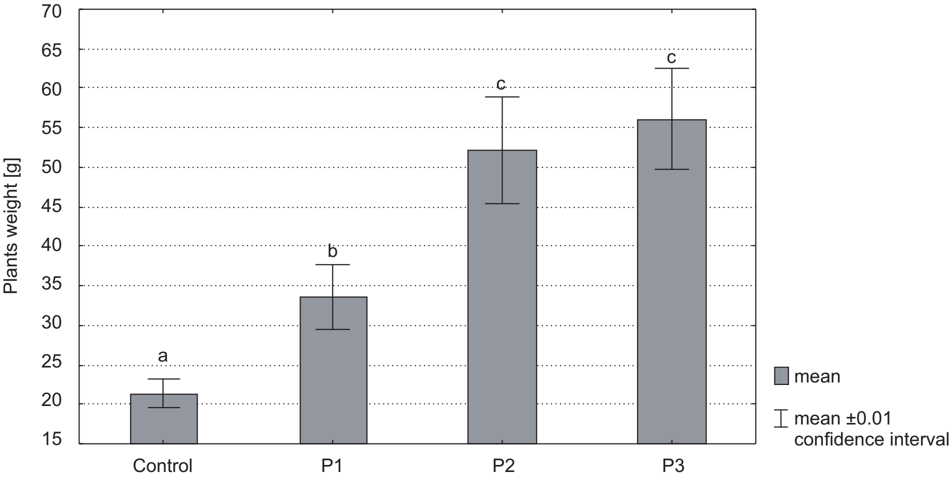

Fig. 1. Plants weight per pot (data destinated with same letters do not differ significantly at $P \leq 0.01$)

The biomass obtained from a single pot increased proportionally to the level of fertilization (Fig. 1). The P1 level fertilization regime raised the yield of Virginia fanpetals by 57 %, while the P2 level increased the yield by 2.5-fold relative to the control. Although the subsequently higher fertilization doses raised the yield of biomass, the increment was not significant. In a study reported by Borkowska et al [32], the level of fertilization with nitrogen (100 and 200 kg · ha^{-1}) had no effect on yield of Virginia fanpetals biomass, while the phosphorus fertilization significantly increased biomass yields as the owing to the more intensive branching and increased height of the plants.

Conclusions

Ash originating from the incineration of sewage sludge completed at the Lyna Wastewater Treatment Plant in Olsztyn is characterized by a high mineralization rate and a markedly alkaline reaction. Phosphorus and calcium are dominant fertilizing elements. The content of cadmium and lead is below the permissible levels set for these metals in mineral fertilizers. Ash from incinerated sewage sludge used as a substitute of phosphorus fertilizers did not have any notable effect on the soil content of the mobile forms of cadmium, copper, lead and chromium. With respect to nickel, zinc and manganese, the medium and high rates of fertilizing ash significantly increased the content of these metals in soil. The yield of Virginia fanpetals and its content of nitrogen, phosphorus and potassium increased in proportion to the increasing doses of ash. The rate of ash, however, did not affect the concentration of sodium or magnesium in plants, but after an application of the highest rate of ash the plant content of calcium increased significantly. Ash modified the content of heavy metals in the plant material only very slightly.

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WYKORZYSTANIE POPIOŁÓW ZE SPALANIA KOMUNALNYCH OSADÓW ŚCIEKOWYCH DO NAWOŻENIA ŚLAZOWCA PENSYLWAŃSKIEGO

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Abstrakt: Celem pracy było określenie wpływu popiołu ze spalania osadów ściekowych na plon i skład mineralny ślazowca pensylwański oraz na zawartość metali ciężkich w glebie. Podstawę badań stanowiło doświadczenie wazonowe, w którym popiół ze spalania osadów ściekowych z oczyszczalni „Łyna" w Olsztynie był stosowany jako substytut nawozów mineralnych. W popiele tym dominującymi składnikami nawozowymi były fosfor i wapń. Zawartość kadmu i ołowiu była niższa od dopuszczalnych stężeń tych metali w nawozach mineralnych. Popiół ze spalania osadów ściekowych nie miał istotnego wpływu na zawartość w glebie z mobilnych form kadmu, miedzi, ołowiu i chromu. Średnie i wysokie dawki popiołu znacznie zwiększyły w glebie zawartość cynku, niklu i manganu. Dawki popiołu nie miał wpływu na zawartość sodu i magnezu w roślinach, natomiast największa dawka popiołu istotnie zwiększyła zawartość wapnia w roślinach. Popiół tylko nieznacznie modyfikował zawartości metali ciężkich w materiale roślinnym.

Słowa kluczowe: popiół ze spalania komunalnych osadów ściekowych, ślazowiec pensylwański, fosfor, metale ciężkie, gleba

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MICROBIOLOGICAL CONTAMINATION OF FOOD

MIKROBIOLOGICZNE ZANIECZYSZCZENIA ŻYWNOŚCI

Abstract: The aim of the study was the statistical analysis of available data of microbiological investigation of food products. Data for the analysis were provided by the sanitary-epidemiological stations in Swietokrzyskie voivodship in 2008–2011. The different types of food products (meat, dairy products, grains products, fish, vegetables, fruit, water, soft drinks, vegetable fats, herbs, coffee, tea, cocoa, foodstuffs intended for particular nutritional uses and nutritional supplements) were studied. The research material was obtained from the products of national origin, food imported with distinguishing between the products originating from the European Union. The presence of *Listeria monocytogenes*, *Escherichia coli*, *Salmonella* spp. and *Yersinia enterocolitica* was analyzed. *Escherichia coli* and *Yersinia enterocolitica* were detected sporadically. *Listeria monocytogenes* was detected the most frequently in confectionery products, convenience foods, milk and milk products, most rarely in fruits and vegetables. It has been shown that the most frequent pathogens in food samples were *Salmonella* spp., also responsible for the largest number of food poisoning in Poland. *Salmonella* spp. were detected primarily in domestic products. The increase of the prevalence of those bacteria was observed during next years (2008–2011). It should be emphasized, that all of the analyzed samples contained at least one of the studied species. Food contamination may cause an increase of food poisoning incidents as well as others diseases caused by these pathogenic bacteria. It is important to observe rules of hygiene during the production, preparation and consumption of food products, but this problem is more complex.

Keywords: food contamination, epidemiology

Introduction

The presence of microorganisms in food products may have an beneficial or adverse effect for human health. For a long time, bacteria are used for food production, *eg* milk products, bread, beer and other alcohols. Bacteria are present in almost every sold food product. In the present study we focus on an assessment of microbial contaminants in food. In the early seventies of the last century, food contamination has significantly increased. The main reason was the development of industry and agriculture. It also has

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an impact on the epidemiological situation in Poland [1]. The climatic conditions in Poland are conducive to the development of agriculture. This development is associated with overproduction of sewage, excessive use of organic fertilizers and organic-mineral fertilizers [2]. Food is monitored primarily in terms of heavy metal concentration, the amount of pesticides and nitrates, the presence of antibiotics and microbial contamination. Consumption of contaminated food poses a high risk of serious food poisoning which may lead to death [3]. Food poisoning can be divided into chemical and biological origin. Poisoning of chemical basis are usually caused by preservatives, dyes, antibiotics and pesticides. Chemical contamination poses a threat to the entire society, while microbiological contaminants threaten on groups of persons belonging to young, old, pregnancy and ill (YOPI). People belonging to YOPI have to pay particular attention to the quality of nutrition and consumed products. Poisoning of biological origin are caused by viruses, parasites, protozoa, fungi, bacteria and bacterial toxins [4]. In Poland, food poisoning is a serious epidemiological problem especially during the summer and early autumn. High temperatures and the touristic migration of people makes it difficult to preserve food hygiene, storage and food production. In spite of different etiologies, bacterial poisoning are characterized by common symptoms: diarrhea, abdominal pain, nausea, vomiting, dizziness, increased body temperature, weakness and dehydration [5]. The most important etiological factors include endotoxin of *Salmonella* spp., *Staphylococcocus* sp., botulinum toxin produced by *Clostridium botulinum*, less frequently *Clostridium perfringens* type A toxins. Bacteria classified as opportunistic pathogens as *Escherichia coli*, *Proteus vulgaris*, *Bacillus cereus* and other are also important etiological factor of food contamination [6]. Food is the optimal environment for the growth of microorganisms. The number and species composition of microorganisms depend on the environmental conditions that stimulate or inhibit their growth. The basic agents include water activity, temperature, air relative humidity, pH of environment, residual pressure, the availability of oxygen, the presence of salt (cations and anions) [7]. Due to the specific conditions of growth of pathogenic microorganisms, the microbiological food analysis is carried out by several methods. The analyzes are conducted in accordance with the guidelines described in the standard PN-ISO 4832:2007. Full screening of food needs to determine the essential etiological factors: the number of mesophilic aerobic microorganisms grown at 30 ^{o}C (PN-EN ISO 4833:2004+Apl:2005), the number of coagulase-positive staphylococci grown in 37 ^{o}C (PN-EN ISO 6888-1:2001+Al:2004), the number of presumptive *Bacillus cereus* grown at 30 ^{o}C (PN-EN ISO 7932:2005), the presence of *Listeria monocytogenes* (PN-EN ISO 11290-1:1999+ A1:2005; PN-EN ISO11290-2:2000+A1:2005+A1:2006+Ap2:2007), the number of beta-glucuronidase-positive *Escherichia coli* growing in 44 ^{o}C (PN-ISO 16649-2:2004), the presence of *Enterobacteriacae* growing at 37 ^{o}C (PN-ISO 21528-1:2005 P.4.1; PN-ISO 21528-2:2005), the number of mold and yeast cultured at 25 ^{o}C (PN-ISO 21527-1:2009; PN-ISO 21527-2:2009). Due to the widespread occurrence of microorganisms in food, food poisoning caused by biological factors will be always recorded. Proper storage and ensure hygiene during the production may reduce the risk of infection to a minimum. Control of food processing facilities should be done as often as possible to minimize the risk of getting contaminated food products to consumer.

Materials and methods

The research materials were the data available from three sanitary-epidemiological stations in Kielce, Busko-Zdroj and Sandomierz in Swietokrzyskie voivodship. The food analysis presence of *Salmonella* spp., *Listeria monocytogenes*, *Escherichia coli* and *Yerenia enterocolitica*. All samples were collected in accordance with the standards in force in Poland. In all stations, analyzed samples belonged to meat products, dairy products, grains products, fish, vegetables, fruit, water, soft drinks, vegetable fats, herbs, coffee, tea, cocoa, foodstuffs intended for particular nutritional uses and nutritional supplements. The statistical analyzes were performed by GraphPad Prism v.6.

Results and discussion

The aim of this study was the investigation of food products based on the presence of pathogenic bacteria. Analysis of food samples was carried out by three sanitary-epidemiological stations in Swietokrzyskie voivodship. This allows to illustrate the local problem of infections of food products over several years.

The available results of microbiological analysis represent prevalence of *Salmonella* spp., *Listeria monocytogenes* and *Escherichia coli* in food samples, in 2009 and 2011. The data were made available by sanitary-epidemiological station in Busko-Zdroj in Swietokrzyskie voivodship. Analyzing the data carefully, the number of positive samples with bacteria *Salmonella* spp., and *Listeria monocytogenes* decreased by 27 % and 32 % respectively. The presence of *Escherichia coli* in food increased by 1.45 fold in 2011. The frequency of identified bacteria in the food was comparable or diverse between these two years. It was depended on the type of food (Fig. 1).

Salmonella spp. was identified in almost all types of products. Exemption was water and soft drinks. The highest number of samples (more than 50) were tested from the groups of product such as: milk and dairy products, confectionery and vegetables. According to data confectionery products were contaminated by *Salmonella* spp. in 100 % of studied samples. *Salmonella* spp. was found in total number of samples of poultry, eggs and eggs products, grain and grain products, coffee, tea cocoa, delicatessen products and nutritional supplements. It is known that *Salmonella* spp. are commonly found in chicken eggs, chicken and pork meats [8]. All product groups in which *Salmonella* was found seem to be associated with these typical sources of infection [9].

In this study, the number of pathogens detected in food in three sanitary stations in Swietokrzyskie voivodship was analyzed. In all cases it was found, that the most contaminated products included confectionery, milk and milk products. As mentioned above, the most frequently identified species was *Salmonella* spp. The frequent occurrence of this species in milk and milk products was also observed in other countries. For example, *Salmonella* spp. was identified in 27 % of fresh cheese in

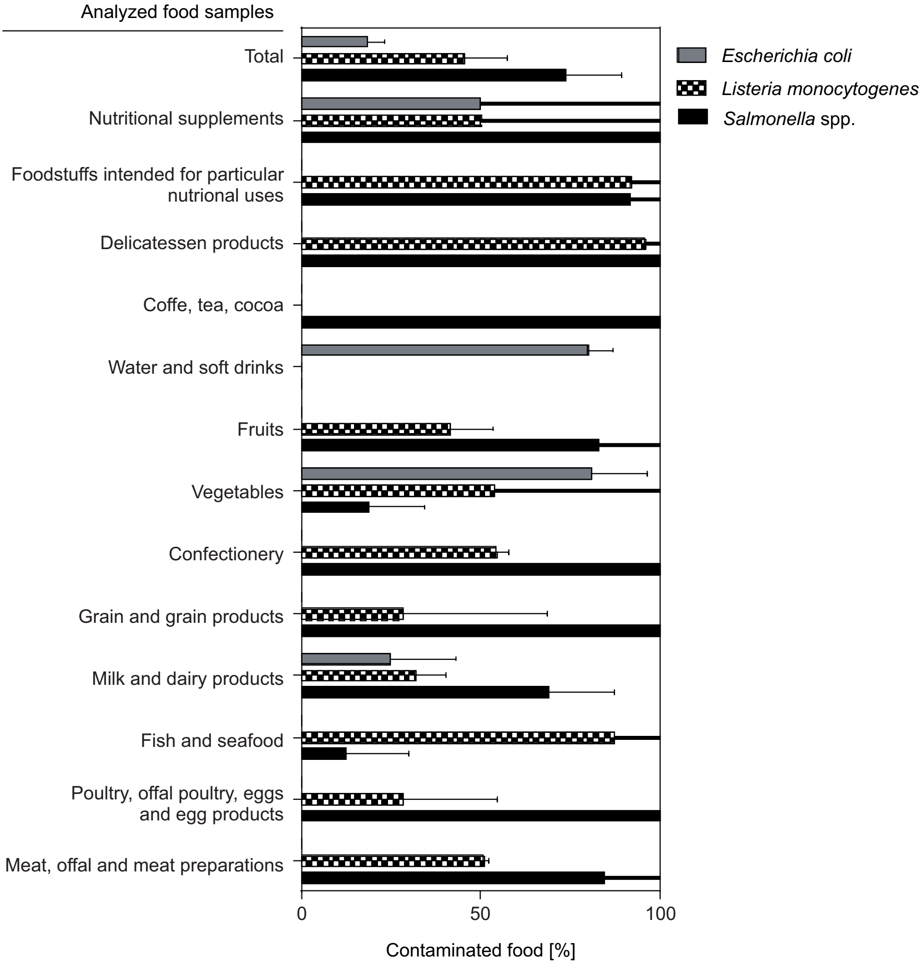

Fig. 1. Percent of food contaminated by particular bacteria (*Escherichia coli*, *Listeria monocytogenes*, *Salmonella* spp.) in Busko Zdroj (Swietokrzyskie voivodship) in 2009 and 2011 compared to total analyzed food samples

Mexico. In the same cheese, *Escherichia coli* was identified in 10 % of samples [10]. In the case of milk and milk product samples tested in Swietokrzyskie voivodship, *Salmonella* spp. was detected in 82 % of analyzed products. Such a large percentage of occurrence may result from the diversity of milk products examined in Swietokrzyskie voivodship. *Salmonella* spp. was also found in 12 % of vegetables samples. It is three times less than in the case of vegetables tested for the presence of *Salmonella* spp. in Malaysia [11]. This could be due to different climatic conditions and the sanitary state of individual countries Traditional physical process of food decontamination (Thermal pasteurization) can eliminate most of vegetative microorganisms (*eg Salmonella*) causing food-borne diseases [12]. Therefore, despite the high prevalence of *Salmonella* in a food product the risk of infection can be easily reduced by the appropriate preparation of the food. Another pathogen detected in food is *Escherichia coli*. In this study, the presence of *E. coli* was the most frequent detected in vegetables and fruits. It could resulted from fecal contamination of domestic or wild animals during cultivation or handling [13]. The results presented in this work show also that the most contaminated products were animal origin (meet, milk and milk products). *E. coli* can adapt to adverse environmental conditions. Data prove that *Escherichia coli* can growth in the presence of Biocides which are compounds commonly used in the food system as poultry decontaminants (*eg* trisodium phosphate) to reduce or eliminate both pathogenic and spoilage micro-organisms [14]. *Salmonella* spp. and *E. coli* were the most frequently detected bacteria in a food product, what could generated a serious risk of epidemics.

We also examined the incidence of *Listeria monocytogenes* in food products. The presence of *L. monocytogenes* was found in all product groups except water and soft drinks, coffee, tea, cocoa. The largest amount was found in processed foods as well as in fish. According to the literature, *L. monocytogenes* in relatively large quantities is present in certain food groups, such as soft cheese, unpasteurized milk, ice cream, various types of meat such as: fermented meats, sausages, hot dogs, turkey, ham RTE (ready-to-eat) and seafood products, among others, smoked cold or warm salmon, shrimp, clams, pickles, fish salads. *L. monocytogenes* is also found in many types of vegetables, fruits and fruit juices [8, 15–17].

Another source of data came from Sanitary-Epidemiological Station in Kielce operates on the whole territory of province. The results provide the overall epidemiological status in Swietokrzyskie voivodship in 2010. The research material was obtained from the products of national origin, food imported with distinguishing between the products originating from the European Union. The data show, that the most polluted were the products of national origin. The most frequently detected bacteria was *Salmonella* spp. The presence of *Salmonella* spp. was detected in 1320 analyzed samples, *Escherichia coli* in 277 samples, *Yersinia enterocolitica* in 51 samples. Based on data from the sanitary – epidemiological station, the frequency of food poisoning incidents caused by bacteria in 2010 was analyzed (Fig. 2). The most common food poisoning was caused by *Escherichia coli*. This pathogen caused illnesses in 18 % of cases. *Yersinia enterocolitica* caused poisoning in 15 % of cases and *Salmonella* spp. – 5 %. According to literature, the pathogenicity of *Y. enterocolitica* and *E. coli* is characterized by a presence of virulence factors, which give a high morbidity in humans, even in small concentration of bacteria in the body [18]. In this study, we observed that *Salmonella* spp. caused infection three time less than *E. coli* and *Y. enterocolitica.* This can be due to the fact, that emergence of infection requires high infective dose of cells, what amounts to 10^6–10^8 cells [18].

Similar analysis were made available from Sanitary – Epidemiological Station in Sandomierz. The presence of microbiological indicator were studied in food products in 2008–2010. Samples were collected from all over the city. The increase of number of poisoning caused by *Listeria monocytogenes* was observed in 2009 and 2010. Despite of absence of data of mortality or poisoning caused by *L. monocytogenes* in Swietokrzyskie voivodship, the high number of detected pathogens was observed in

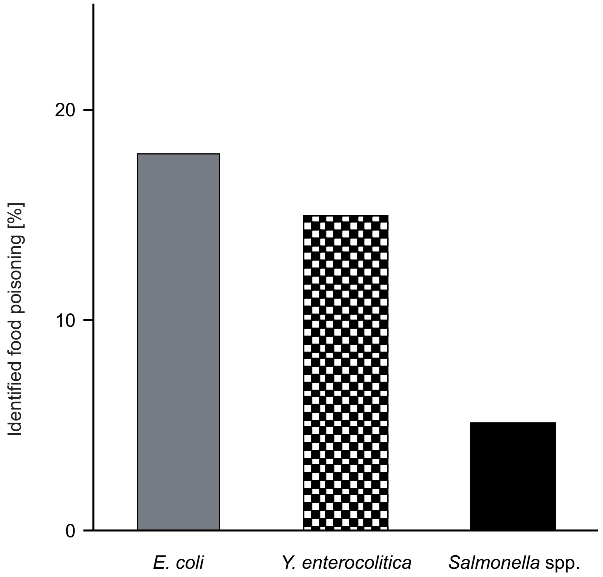

Fig. 2. Percent of food poisoning cases induced by bacteria detected in examined food samples in 2010 in Swietokrzyskie voivodship

2009 (Fig. 1). In 2011, the number of cases has decreased. This phenomenon is observed also in all over the world in recent years [19, 20]. Currently, infections caused by *Listeria monocytogenes* are regarded as a serious threat, because it is characterized by a high mortality rate 20–30 % [21]. In the EU, the proportion of patients with listeriosis has increased by 19.1 % in 2009 in comparison to 2008. In 2009, 1,601 positive cases were recorded, this level remained also in 2010. In 2009, *L. monocytogenes* led to 270 deaths. Meanwhile in the United States microorganism was the cause of 2,500 cases, 2,289 hospitalizations and 449 deaths. Listeriosis is therefore one of the deadly food-borne illness reported in the United States or countries of European Union [8, 22, 23].

It was found, that all analyzed food samples possessed at least one of analyzed bacterial pathogen. It should be emphasized, that the presence of pathogenic bacteria in food is not necessary to illness after consumption. Every organism has defense mechanisms which prevent bacterial infection. Ability to defend is individual feature of the species it and determines the occurrence of disease [24–28].

Conclusions

The most common pathogen detected in food was *Salmonella* spp., also responsible for the largest of the number of cases in Swietokrzyskie voivodship. *Escherichia coli* was identified in meat, milk and dairy products, also in water and soft drinks. In 2009 and 2011, an increase of the *Listeria monocytogenes* positive samples detected in food product were observed.

Acknowledgements

We thank sanitary – epidemiological stations in Swietokrzyskie voivodship for providing source material for the analysis. We would like to thank also Diana Berlinska, Wioleta Nowaczek and Ewelina Sokolowska for technical support.

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MIKROBIOLOGICZNE ZANIECZYSZCZENIA ŻYWNOŚCI

Katedra Ochrony i Kształtowania Środowiska
Uniwersytet Jana Kochanowskiego w Kielcach

Abstrakt: Celem pracy była analiza produktów żywnościowych na podstawie obecności patogennych mikroorganizmów. Dane do analizy zostały dostarczone przez stacje sanitarno-epidemiologiczne w województwie świętokrzyskim w latach 2008–2011. Badano różne rodzaje produktów spożywczych (mięso, produkty mleczne, produkty zboża, ryby, warzywa, owoce, woda butelkowana, napoje bezalkoholowe, tłuszcze roślinne, zioła, kawa, herbata, kakao, środki spożywcze specjalnego przeznaczenia żywieniowego oraz suplementy diety). Materiał badawczy pochodził z produktów pochodzenia krajowego oraz z importu z rozróżnieniem produktów pochodzących z Unii Europejskiej. Analizowano obecność takich bakterii, jak: *Listeria monocytogenes*, *Escherichia coli*, *Salmonella* spp. i *Yersinia enterocolitica*. *Escherichia coli* i *Yersinia enterocolitica* były wykrywane sporadycznie. Wykazano, że najczęściej występującym patogenem w próbkach żywnościowych pochodzenia krajowego były bakterie z grupy *Salmonella* spp., które są odpowiedzialne za największą liczbę zatruć pokarmowych w Polsce. Równie często wykrywano *Listeria monocytogenes*, szczególnie w produktach cukierniczych, garmażeryjnych, mleku i produktach mlecznych, a najrzadziej w owocach i warzywach. Niestety zaobserwowano wzrost częstości występowania tych bakterii w kolejnych latach (2008–2011). Należy podkreślić, że wszystkie analizowane próbki zawierały co najmniej jeden z badanych gatunków. Zanieczyszczenie żywności może spowodować wzrost przypadków zatruć pokarmowych, a także innych chorób wywołanych przez te bakterie chorobotwórcze. Ważne jest, aby przestrzegać zasad higieny podczas produkcji, przygotowania i konsumpcji produktów żywnościowych. Problem ten jest jednak bardziej złożony.

Słowa kluczowe: skażenie żywności, epidemiologia

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WWTP – oczyszczalnia ścieków płynnych (3) 297, *24*

Varia

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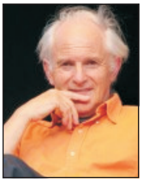

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The Climate Change Crisis?

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Monitoring long-term and large-scale deposition of pollutants based on moss analyses

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Eiliv STEINNES
Norwegian University of Science and Technology, Trondheim, NO
Influence of precipitation chemistry on the mobility of trace substances in boreal forest soils: radiocaesium as an example

Piotr P. WIECZOREK
Opole University, Opole, PL
Estrogens and xenoestrogens as emerging environmental contaminants

SHORT CONFERENCE REPORT

The Conference ECOpole '15 was held in 14–17 X 2015 in Hotel Ziemowit in Jarnoltowek, PL. It was the twenty forth ecological conference of the series of meetings organised by the Society of Ecological Chemistry and Engineering, Opole, PL.

122 participants, including delegates representing following countries: Czech Republic, Germany, Great Britain, Hungary, Norway, Poland, Romania, Russian Federation, and United States of America took part in the event and presented 29 oral contributions and 111 posters.

The Abstracts of the Conference contributions were and are available on the Conference website

ecopole.uni.opole.pl

The Conference Agenda was divided into 4 sections:

– SI Ecological Chemistry and Engineering
– SII Environment Friendly Production and Use of Energy
– SIII Forum of Young Scientists and Environmental Education
– SIV Health, Ecology and Agriculture.

The Conference issue of the quarterly *Ecological Chemistry and Engineering S* containing among others Keynote Speakers papers, was distributed at the Conference Reception desk together with a CD-ROM (containing short info on Keynote Speakers, Abstracts of the Conference presentations as well as ECOpole '15 Conference Programme).

On Wednesday (14th October 2015) at 19.00 a brief Opening Ceremony was performed by prof. Maria Wacławek, (Chairperson of the Organising Committee) and prof. Witold Wacławek, (Chairman of the Conference Scientific Board and President of the Society of Ecological Chemistry and Engineering). Just afterwords the Conference participants attentively listened to the Opening Lecture:

***The Climate Change Crisis*?**

by the **Nobel Prize Winner in Chemistry 2006 Professor Sir Harold Walter KROTO** (The Florida State University, Tallahassee, Florida, USA).

After the lecture **video conference with Professor H.W. Kroto** was organised and a number of issues were raised and discussed *eg* what is:

– the most dangerous contamination generated by the humankind;
– the progress and rate in sustainable development;

– the way for future improvements in environmental education and how to stop global warming.

During the conference the plenary lectures were also delivered by other invited lecturers: **Marina V. FRONTASYEVA** (Frank Laboratory of Neutron Physics Joint Institute for Nuclear Research, Dubna, RU): *Monitoring long-term and large-scale deposition of pollutants based on moss analyses*, **Bogusław BUSZEWSKI** (Faculty of Chemistry and Center for Modern Interdisciplinary Technologies – BioSep, Toruń, PL): *A new approach in identification of biomarkers for early cancer detection*, **Josef JAMPÍLEK** (University of Veterinary and Pharmaceutical Sciences Brno, CZ): *Applications of nanoformulations in agricultural production and their potential impact on food and human health*, **Eiliv STEINNES** (Norwegian University of Science and Technology, Trondheim, NO): *Influence of precipitation chemistry on the mobility of trace substances in boreal forest soils: radiocaesium as an example* and **Piotr P. WIECZOREK** (Opole University, Opole, PL): *Estrogens and xenoestrogens as emerging environmental contaminants*.

There were also presented very interesting lectures, eg by **Z.A. Szydło** (Highgate School, London, UK): *The life and work of professor Jan Czochralski (1885–1953*), **Á. Bálint** (Óbuda University, Institute of Environmental Engineering, Budapest, Hungary): The effect of heavy metals to be found in the environment on the human body, **A.I. Stoica** (University of Bucharest, Bucharest, RO): *The influence of gold mining industry on the pollution of Rosia Montana District*, **S. Fränzle** (Zittau International School, part of Dresden Tech (TUD) [central scientific unit], Zittau, FR, D): *Chitin as a novel polymeric vector for biomonitoring – understanding the basic chemical features of adsorption and the ecosystems-observation features simultaneously*, **J. Kříž** (University of Hradec Králové, Hradec Králové, CZ): *Examples of continuous monitoring in health care: bed exit alarm and intracranial pressure*, **D. Panasiuk** (Cardinal Stefan Wyszyński University in Warsaw, Warszawa, PL): *Substance flow analysis for mercury in Poland for year 2013* and **A. Zaremba** (Czestochowa University of Technology, Częstochowa, PL): *On the efficiency of working Renewable Energy Sources installations*. With the last lecture is closely connected an excursion in Hotel Ziemowit – to visit working Renewable Energy Sources (RES) Installations (solar cells, collectors and heat pumps) – it was organized as the last point of the scientific program for Thursday (it started at 6.30 p.m.).

Thursday, it was Conference day of hard work. It also included the second Poster Session with 31 presentations. Many of the discussions started at the posters, lasted until the evening hours.

As usually during the ECOpole Conferences, the second day included the Session of the Young Scientists (a forum of young scientists that present and discuss local ecological problems of their countries). During the Young Scientists' and Environmental Education Poster Session 34 posters were presented.

The Scientific Board: **Grzegorz Wielgosiński** (Lodz University of Technology, Łódz, PL), **Marina V. Frontasyeva** (Frank Laboratory of Neutron Physics Joint Institute for Nuclear Research, Dubna, RU), **Daniela Szaniawska** (Maritime University of Szczecin, Szczecin, PL) and **Eiliv Steinnes** (Norwegian University of Science and

Technology, Trondheim, NO) granted awards (sponsored by the Society of Ecological Chemistry and Engineering) for the best presentations. The awards for oral presentations were given to: **Anna Kwiecińska** Ph.D., Eng. (Institute for Chemical Processing of Coal, Zabrze, PL) for the lecture: **A. Kwiecińska, T. Iluk, S. Stelmach:**: *The application of membrane processes in the utilization of wastewater generated during biomass gasification*, **Krzysztof Rajczykowski** M. Sc., Eng. (Silesian University of Technology, Gliwice, PL) for the presentation: **K. Rajczykowski, O. Sałasińska, K. Loska**: *Chemical modification of biosorbents as a method of increasing the efficiency of selected metals biosorption processes from aqueous solutions* and **Monika Janas** M. Sc., Eng. (Lodz University of Technology, Łódz, PL) for the lecture: **M. Janas, A. Zawadzka**: *Energy willow from experimental plantation as potentially clean energy source*.

The awards for poster presentations were given to: **Edyta Kudlek** M. Sc., Eng. (Silesian University of Technology, Gliwice, PL) for the poster: **E. Kudlek, J. Bohdziewicz, M. Dudziak**: *Influence of water matrix on the retention of selected pharmaceutical compounds by high-pressure membrane filtration*, **Paulina Rdzanek** M. Sc., Eng. (Lodz University of Technology, Łódz, PL) for the poster **P. Rdzanek, J. Marszałek, W. Kamiński**: *The butanol-ethanol-acetone-water recovery by pervaporation using commercial membranes* and **Urszula Wydro** M. Sc., Eng. (Bialystok University of Technology, Białystok, PL) for the poster: **U. Wydro, E. Wołejko, B. Pawluśkiewicz, T. Łoboda**: *The influence of fertilization with sewage sludge on growth and grasses biodiversity in urban areas.*

On Saturday morning an excursion was organised to the **Museum in Zlate Hory**.

Closing the conference, prof. Maria and Witold Wacławek made short recapitulation. In general, ECOpole '15 was focused on monitoring of the quality of natural environment, its effects on human life, environmental education as well as application of renewable sources of energy.

They expressed gratitude to all participants for coming and taking active part in the Conference and thanked Sponsor (Ministry of Science and Higher Education, Warszawa, PL) as well as all Chairpersons of Sessions.

The organizers informed that the electronic version of the presented contributions (lecture or poster) could be published on the Conference website. They announced, that full texts of the presented papers will be published (after obtaining reviewers' positive opinions) in the successive issues of the journals *Ecological Chemistry and Engineering A* and *S* and they will be distributed to all participants. The Extended Abstracts of the presentations will be published in two subsequent issues of semi-annual *Proceedings of the ECOpole*.

At the end they invited all Colleagues to attend the ECOpole'16 Conference, which will be held in Hotel Antałówka in Zakopane, PL in the next October.

Maria Wacławek

SPRAWOZDANIE
z Środkowoeuropejskiej Konferencji ECOpole'15

W dniach 14–17 października 2015 r. odbywała się w Jarnołtówku XXIV Środkowoeuropejska Konferencja ECOpole '15, zorganizowana przez Towarzystwo Chemii i Inżynierii Ekologicznej (TChIE). Uczestniczyły w niej 122 osoby reprezentujące Anglię, Czechy, Federację Rosyjską, Niemcy, Norwegię, Polskę, Rumunię, Stany Zjednoczone Ameryki i Węgry, które przedstawiły 29 referatów oraz 111 posterów na 4 sesjach posterowych.

Każdy z uczestników otrzymał w teczce konferencyjnej zeszyty kwartalnika *Ecological Chemistry and Engineering S* oraz *Proceedings of ECOpole,* a także CD-ROM z krótkimi informacjami o zaproszonych wykładowcach, abstraktami wystąpień oraz programem konferencji. Abstrakty wystąpień były i są dostępne na stronie webowej konferencji

ecopole.uni.opole.pl

Podobnie jak w latach poprzednich, konferencja ECOpole'15 była poświęcona różnym aspektom ochrony środowiska przyrodniczego. Jej obrady były zgrupowane w czterech Sekcjach:

- SI Substancje chemiczne w środowisku przyrodniczym oraz ich monitoring
- SII Odnawialne źródła energii i jej oszczędne pozyskiwanie oraz użytkowanie
- SIII Forum Młodych (FM) i Edukacja proekologiczna
- SIV Wpływ zanieczyszczeń środowiska oraz żywności na zdrowie ludzi.

W środę (14.10.2015 r.) o godz. 19.00 konferencję otworzyli prof. Maria Wacławek (Uniwersytet Opolski) – przewodnicząca Komitetu Organizacyjnego i prof. Witold Wacławek (Towarzystwo Chemii i Inżynierii Ekologicznej, Opole) – przewodniczący Rady Naukowej Konferencji i prezes TChIE. Uczestnicy konferencji z uwagą wysłuchali referatu inauguracyjnego **Laureata Nagrody Nobla z Chemii w 2006 r. Prof. Sir Harolda Waltera KROTO** (The Florida State University, Tallahassee, Florida, USA):

The Climate Change Crisis?

Zaraz po nim rozpoczęła się wideokonferencja z prof H.W. Kroto. W czasie jej trwania dyskutowano między innymi nad.:

- najbardziej niebezpiecznymi zanieczyszczeniami generowanymi przez człowieka;
- postępem i kierunkami zrównoważonego rozwoju;

– jak można doskonalić edukację ekologiczną i czy można zatrzymać globalne ocieplenie.

W czwartek Sesję Plenarną rozpoczęły wykłady **prof. Bogusława BUSZEWSKIEGO** (Centrum Edukacyjno-Badawcze Metod Separacyjnych i Bioanalitycznych BioSep, Uniwersytet im. Mikołaja Kopernika, Toruń): *A new approach in identification of biomarkers for early cancer detection* oraz **prof. Piotra P. WIECZORKA** (Uniwersytet Opolski, Opole): *Estrogens and xenoestrogens as emerging environmental contaminants*.

Po Sesji Plenarnej odbyła się pierwsza Sesja Posterowa, na której zaprezentowano 28 prac. Podczas konferencji wykłady plenarne wygłosili również inni zaproszeni wybitni profesorowie: **Marina V. FRONTASYEVA** (Frank Laboratory of Neutron Physics Joint Institute for Nuclear Research, Dubna, RU): *Monitoring long-term and large-scale deposition of pollutants based on moss analyses,* **Josef JAMPÍLEK** (University of Veterinary and Pharmaceutical Sciences Brno, CZ): *Applications of nanoformulations in agricultural production and their potential impact on food and human health*, **Eiliv STEINNES** (Norwegian University of Science and Technology, Trondheim, NO): *Influence of precipitation chemistry on the mobility of trace substances in boreal forest soils: radiocaesium as an example*.

Ponadto bardzo interesujące referaty przedstawili: **Z.A. Szydło** (Highgate School, London, UK): *The life and work of professor Jan Czochralski (1885–1953*), **Á. Bálint** (Óbuda University, Institute of Environmental Engineering, Budapest, Hungary): The effect of heavy metals to be found in the environment on the human body, **A.I. Stoica** (University of Bucharest, Bucharest, RO): *The influence of gold mining industry on the pollution of Rosia Montana District*, **S. Fränzle** (Zittau International School, part of Dresden Tech (TUD) [central scientific unit], Zittau, FR, D): *Chitin as a novel polymeric vector for biomonitoring – understanding the basic chemical features of adsorption and the ecosystems-observation features simultaneously*, **J. Kříž** (University of Hradec Králové, Hradec Králové, CZ): *Examples of continuous monitoring in health care: bed exit alarm and intracranial pressure*, **D. Panasiuk** (Uniwersytet Kardynała Stefana Wyszyńskiego Warszawa): *Substance flow analysis for mercury in Poland for year 2013* i **A. Zaremba** (Politechnika Częstochowska, Częstochowa): *On the efficiency of working Renewable Energy Sources installations*. Spotkały się one z dużym zainteresowaniem uczestników.

Ostatnim punktem czwartkowego programu naukowego była wycieczka po Hotelu Ziemowit (rozpoczęła się o 18:30). Była ona ściśle związana z ostatnim tego dnia wykładem – jej uczestnicy mogli zobaczyć pracujące instalacje z odnawialnymi źródłami energii (ogniwa słoneczne, kolektory i pompy ciepła), których sprawność analizowano na wystąpieniu.

W czwartek po południu odbyła się druga z kolei Sesja Posterowa. Zaprezentowano na niej 31 plakatów. Wiele dyskusji rozpoczętych przy posterach kontynuowano do późnych godzin wieczornych.

O godzinie 20.00 uczestnicy konferencji zostali zaproszeni na uroczystą kolację.

W piątek po południu tradycyjnie odbywało się Forum Młodych (FM). Młodzi ekolodzy, w czasie swoich wystąpień (było ich 12) dyskutowali nad lokalnymi problemami ekologicznymi swoich krajów. W czasie Sesji Posterowej Forum Młodych, zaprezentowano 34 plakaty.

Jury w składzie: **prof. Grzegorz Wielgosiński** (Politechnika Łódzka, Łódź) – przewodniczący, **prof. Marina V. Frontasyeva** (Frank Laboratory of Neutron Physics Joint Institute for Nuclear Research, Dubna, RU), **prof. Daniela Szaniawska** (Akademia Morska w Szczecinie, Szczecin) i **prof. Eiliv Steinnes** (Norwegian University of Science and Technology, Trondheim, NO) przyznało nagrody młodym pracownikom naukowym.

I nagrodę przyznano **dr inż. Annie Kwiecińskiej** (Instytut Chemicznej Przeróbki Węgla, Zabrze) za referat: **A. Kwiecińska, T. Iluk, S. Stelmach**: *The application of membrane processes in the utilization of wastewater generated during biomass gasification.* II nagrodę uzyskał **mgr inż. Krzysztof Rajczykowski** (Politechnika Śląska Gliwice) za prezentację ustną: **K. Rajczykowski, O. Sałasińska, K. Loska**: *Chemical modification of biosorbents as a method of increasing the efficiency of selected metals biosorption processes from aqueous solutions*. III nagrodę przyznano **mgr inż. Monice Janas** (Politechnika Łódzka, Łódź) za referat: **M. Janas, A. Zawadzka**: *Energy willow from experimental plantation as potentially clean energy source*.

Ponadto przyznano trzy nagrody za plakaty. Otrzymali je: I nagrodę **mgr inż. Edyta Kudlek** (Politechnika Śląska Gliwice) za plakat **E. Kudlek, J. Bohdziewicz, M. Dudziak**: *Influence of water matrix on the retention of selected pharmaceutical compounds by high-pressure membrane filtration*; II nagrodę **mgr inż. Paulina Rdzanek** (Politechnika Łódzka, Łódź) za plakat **P. Rdzanek, J. Marszałek, W. Kamiński**: *The butanol-ethanol-acetone-water recovery by pervaporation using commercial membranes* oraz III nagrodę **mgr inż. Urszula Wydro** (Politechnika Białostocka, Białystok) za plakat **U. Wydro, E. Wołejko, B. Pawluśkiewicz, T. Łoboda**: *The influence of fertilization with sewage sludge on growth and grasses biodiversity in urban areas*.

W sobotę została zorganizowana wycieczka do Muzeum w Zlatych Horach.

Na zakończenie konferencji prof. prof. Maria i Witold Wacławek podziękowali wszystkim uczestnikom za udział, a szczególnie osobom, które wygłaszały referaty oraz przewodniczyły obradom. Słowa gorących podziękowań zostały także skierowane do członków Komitetu Organizacyjnego konferencji za duży, wielomiesięczny wkład ich pracy.

Wszyscy uczestnicy konferencji zostali zaproszeni do publikacji swoich prac. Organizatorzy zapewnili, że pełne artykuły z wystąpień konferencyjnych będą sukcesywnie publikowane w *Ecological Chemistry and Engineering A* oraz *S*. Poinformowali też, że rozszerzone streszczenia ukażą się w półroczniku *Proceedings of ECOpole*.

Organizatorzy konferencji zaprosili wszystkich do udziału w dwudziestej piątej jubileuszowej konferencji ECOpole, która odbędzie się w październiku 2016 r. w Zakopanem. Zapowiedzieli oni, że aktywni uczestnicy Forum Młodych konferencji ECOpole '16 mogą liczyć na znaczne obniżenie opłaty konferencyjnej.

Prof. dr hab. inż. Maria Wacławek
Przewodnicząca Komitetu Organizacyjnego
Konferencji ECOpole '15

INVITATION FOR
ECOpole ’16 CONFERENCE

CHEMICAL SUBSTANCES IN ENVIRONMENT

We have the honour to invite you to take part in the 25th annual Central European Conference ECOpole ’16, which will be held in 5–8.10.2016 (Wednesday–Saturday) in Hotel Antalowka in Zakopane, PL.

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

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

The Conference language is English.

Contributions to the Conference will be published as:

- abstracts on the CD-ROM (0.5 page of A4 paper sheet format),
- extended Abstracts (6–8 pages) in the semi-annual journal *Proceedings of ECOpole*,
- full papers will be published in successive issues of the *Ecological Chemistry and Engineering/Chemia i Inżynieria Ekologiczna* (Ecol. Chem. Eng.) ser. A or S.

Additional information one could find on Conference website:

ecopole.uni.opole.pl

The deadline for sending the Abstracts is **15th July 2016** and for the Extended Abstracts: **1st October 2016**. The actualized list (and the Abstracts) of the Conference contributions accepted for presentation by the Scientific Board, one can find (starting from **31st July 2016**) on the Conference website.

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

At the Reception Desk each participant will obtain abstracts of the Conference contributions as well as the Conference Programme recorded on electronic media (the Programme will be also published on the ECOpole ’16 website).

After the ECOpole ’16 Conference **it will be possible to publish electronic version of presented contributions** (oral presentations as well as posters) on this site.

Further information is available from:
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of ECOpole ’16 Conference
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22. 2013 CEC ECOpole ’13 Jarnołtówek
23. 2014 CEC ECOpole ’14 Jarnołtówek
24. 2015 CEC ECOpole ’15 Jarnołtówek

ZAPRASZAMY DO UDZIAŁU
W ŚRODKOWOEUROPEJSKIEJ KONFERENCJI ECOpole ’16

SUBSTANCJE CHEMICZNE
W ŚRODOWISKU PRZYRODNICZYM
w dniach 5–8 X 2016 r. w hotelu Antałówka w Zakopanem

Będzie to **dwudziesta piąta z rzędu** konferencja poświęcona badaniom podstawowym oraz działaniom praktycznym dotyczącym różnych aspektów ochrony środowiska przyrodniczego.

Doroczne konferencje ECOpole mają charakter międzynarodowy i za takie są uznane przez Ministerstwo Nauki i Szkolnictwa Wyższego. Obrady konferencji ECOpole ’16 będą zgrupowane w czterech Sekcjach:

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

Materiały konferencyjne będą opublikowane w postaci:

- abstraktów (0,5 strony formatu A4) na CD-ROM-ie,
- rozszerzonych streszczeń o objętości 6–8 stron w półroczniku *Proceedings of ECOpole,*
- artykułów: w abstraktowanych czasopismach: *Ecological Chemistry and Engineering*/*Chemia i Inżynieria Ekologiczna* (*Ecol. Chem. Eng.*) ser. A i S oraz w półroczniku *Chemistry – Didactics – Ecology – Metrology* (*Chemia – Dydaktyka – Ekologia – Metrologia*).

Termin nadsyłania angielskiego i polskiego streszczenia o objętości 0,5–1,0 strony (wersja cyfrowa) planowanych wystąpień upływa w dniu 15 lipca 2016 r., a rozszerzonych streszczeń – **1 października 2016 r.** Lista prac zakwalifikowanych przez Radę Naukową Konferencji do prezentacji będzie sukcesywnie publikowana od 31 lipca 2016 r. na stronie webowej konferencji. Aby praca (dotyczy to także streszczenia, które powinno mieć tytuł w języku polskim i angielskim, słowa kluczowe w obydwu językach) przedstawiona w czasie konferencji mogła być opublikowana, jej tekst winien być przygotowany zgodnie z wymaganiami stawianymi artykułom drukowanym w czasopismach *Ecological Chemistry and Engineering* ser. A oraz S, które są dostępne w wielu bibliotekach naukowych w Polsce i za granicą. Zalecenia te są również umieszczone na stronie webowej Towarzystwa Chemii i Inżynierii Ekologicznej:

tchie.uni.opole.pl

Wszystkie nadsyłane prace podlegają zwykłej procedurze recenzyjnej.

Wszystkie streszczenia oraz program konferencji zostaną wydane na CD-ROM-ie, który otrzyma każdy z uczestników podczas rejestracji. Program będzie także umieszczony na stronie webowej konferencji

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Po konferencji będzie możliwość opublikowania elektronicznej wersji prezentowanego wystąpienia (wykładu, a także posteru) na tej stronie.

Prof. dr hab. inż. Maria Wacławek
Przewodnicząca Komitetu Organizacyjnego
Konferencji ECOpole ’16

Wszelkie uwagi i zapytania można kierować na adres:
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"*Ghostwriting*" and "*guest authorship*" are a sign of scientific misconduct. To counteract them, please provide information, for the Editor, on the percentage contribution of individual Authors in the creation of publications (including the information, who is the author of concepts, principles, methods, etc.). Editorial Board believes that the main responsibility for those statements bears the Author sending the manuscript.

In preparation of the manuscript please follow the general outline of papers published in *Ecological Chemistry and Engineering A*, available on the website:

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a sample copy can be sent, if requested.

Papers submitted are supposed to be written in English language and should include a summary and keywords, if possible also in Polish language.

Generally, a standard scientific paper is divided into:

– Introduction: you present the subject of your paper clearly, indicate the scope of the subject, present state of knowledge on the paper subject and the goals of your paper;

– Main text (usually divided into: Experimental – you describe methods used; Results and Discussion);

– Conclusions: you summarize your paper;

– References.

The first page should include the author's (authors') given name(s) without titles or scientific degrees like Prof., Ph.D., etc., their affiliations, phone and fax numbers and their email addresses however, with the corresponding author marked by an asterisk.

It is urged to follow the units recommended by the *Systéme Internationale d'Unites* (SI). Graph axis labels and table captions must include the quantity units.

Symbols recommended by the International Union of Pure and Applied Chemistry (Pure and Appl Chem. 1979;51:1-41) are to be followed. Graphics (drawings, plots) should be supplied in the form of digital vector-type files, *eg* CorelDraw v.9, Excel, Inkscape or at least in a bitmap format (TIF, JPG) 600 DPI. In the case of any query please feel free to contact with the Editorial Office. Footnotes, tables and graphs should be prepared as separate files. References cited chronologically should follow the examples given below:

[1] Lowe DF, Oubre CL, Ward CH. Surfactants and cosolvents for NAPL remediation. A technology practices manual. Boca Raton: Lewis Publishers; 1999.
[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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[6] Hakala M, Nygård K, Manninen S, Huitari S, Buslaps T, Nilsson A, et al. J Chem Phys. 2006:125:084504-1-7. DOI: 10.1063/1.2273627.
[7] Kowalski P. Statistical calibration of model solution of analytes. Ecol Chem Eng A. Forthcoming 2016.

Please remember that every sign in the references counts.

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

Each publication is evaluated by at least two independent Reviewers from outside of the unit. In the case of paper written in a foreign language, at least one of Reviewers is affiliated to a foreign institution other than the Author's work.

As a rule double-blind review process is used (the Author(s) and Reviewers do not know their identities). In any case Editor must be sure that no conflict of interest (direct personal relationships, professional relationships, or direct scientific cooperation in the past two years) occurs between the Reviewer and the Author. Reviewer has to fill in the Reviewers report. On its end must be an explicit request to the approval of the article for publication or its rejection.

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

In the case of any query please feel free to contact with the Editorial Office.

Editors

ACKNOWLEDGEMENT FOR REVIEWERS

PODZIĘKOWANIA DLA RECENZENTÓW

The Editors would like to express their gratitude to the following Reviewers who helped in the peer-review process of the papers considered for publication in the journal *Ecological Chemistry and Engineering A*:

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