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Rafał SZMIGIELSKI[1*] and Krzysztof J. RUDZIŃSKI[1]

ADDITION OF BISULFITE IONS TO METHYL VINYL KETONE AND METHACROLEIN RELEVANT TO ATMOSPHERIC PROCESSES

PRZYŁĄCZANIE ANIONÓW WODOROSIARCZYNOWYCH DO KETONU METYLOWO-WINYLOWEGO I METAKROLEINY O ZNACZENIU DLA PROCESÓW ATMOSFERYCZNYCH

Abstract: Methacrolein and methyl vinyl ketone are highly reactive carbonyls that play a pivotal role in the formation of secondary organic aerosols in the Earth's atmosphere. Both carbonyls are the major products of isoprene oxidation. We show that among the atmospheric sinks of methacrolein and methyl vinyl ketone, the aqueous-phase addition of bisulfite anions to their molecules can be relevant under polluted conditions with the increased presence of sulfur dioxide. We demonstrate that aqueous-phase reactions of methyl vinyl ketone and methacrolein with bisulfite anions lead to the formation of primary and secondary organic hydroxysulfonates which currently are not included in the atmospheric chemistry modelling, but can be relevant in mechanisms explaining the formation and growth of the secondary organic aerosols from atmospheric carbonyls. The rate constants for all aqueous-phase reactions involved were determined. The primary addition of bisulfite anions to methacrolein was found significantly faster than that to methyl vinyl ketone, with rate constants $k_{MAC1f} = 8$ and $k_{MVK1f} = 0.18\ mol^{-1} \cdot dm^3 \cdot s^{-1}$ at room temperatures, respectively. The rate constant for the bisulfite addition to methacrolein was ten times faster than reported in the literature. The kinetic and mass spectrometric analyses revealed that in both cases, the dominating product was the C_4 alpha-hydroxysulfonate (a primary adduct), while the C_4 alpha-hydroxy disulfonate (a secondary adduct or diadduct) was produced only in trace quantities. The primary addition of bisufite anions to methacrolein and methyl vinyl ketone should be considered in atmospheric studies relevant to areas with enhanced presence of sulfur dioxide providing sufficiently high concentrations of bisulfite ions in atmospheric waters.

Keywords: atmospheric processes, secondary organic aerosol, rate constants, electrospray mass spectrometry, LC/MS, isoprene, methacrolein, methyl vinyl ketone, sulfur dioxide, bisulfite addition, carbonyls

Introduction

Methacrolein (MAC) and methyl vinyl ketone (MVK) are primary products of isoprene oxidation in the Earth's atmosphere. The latter is the most abundant

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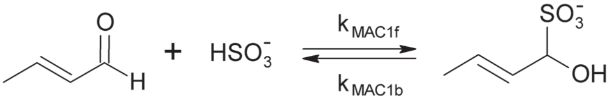
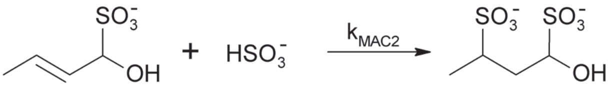
non-methane hydrocarbon emitted to the Earth's atmosphere [1, 2]. Methacrolein and methyl vinyl ketone are the primary products of isoprene oxidation in the gas phase. Smog chamber experiments proved that the process is driven mainly by hydroxyl radicals and to lesser extent by chlorine atoms and ozone [3–6]. Both MAC and MVK undergo further reactions in the atmosphere yielding a number of high molecular weight compounds that significantly contribute to the organic fraction of atmospheric secondary organic aerosols (SOA) [7, 8]. However, the oxidation of isoprene along with subsequent chemical processing of the products thereof is not only restricted to the gas phase but also occurs in the atmospheric waters, *eg* in cloud droplets, by means of hydroxyl and other radicals (*eg*, sulfate radicals) [9–14]. Recently, the once widely recognized then forgotten role of sulfoxy intermediates (*eg*, sulfate radicals) in the atmospheric oxidation of SO_2 was brought back to the first plan [15].

In addition, bisulfite ions HSO_3^- that originate from absorption of SO_2 in water and from dissolution of inorganic sulfites are known to add to carbonyl double bonds in aldehydes and vinyl ketones [16]. The reaction, commonly used in organic synthesis to separate aldehydes and ketones of a small molecular weight from reaction mixtures, was also recalled in the context of atmospheric chemistry [17] and determination of carbonyl compounds in ambient air [18]. The rate constant reported for the addition of HSO_3^- ions to methacrolein at 21 °C was $k_{MAC1f} = 0.65 \pm 0.03\ M^{-1} \cdot s^{-1}$ [19]:

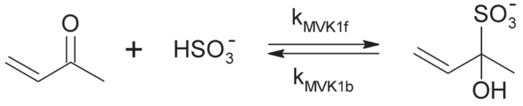


(1a)

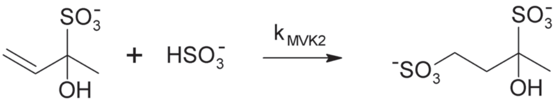


(1b)

The addition of a bisulfite anion to a carbonyl double bond is reversible and leads to the formation of the C_4 alpha-hydroxysulfonate (a primary adduct). The subsequent addition of another anion to a C=C bond, which gives rise to the C_4 alpha-hydroxy-disulfonate (secondary adduct or diadduct), is irreversible and much slower. Methyl vinyl ketone is usually less reactive than methacrolein, so the addition is expected to be slower but follows exactly the same mechanism:



(2a)



(2b)

Generally, bisulfite adducts of methacrolein and methyl vinyl ketone are not included in the atmospheric chemistry modelling, however these processes are expected to be relevant to mechanisms explaining the formation and growth of the secondary organic aerosols from atmospheric carbonyls. In our study, we decided to confirm that aqueous-phase reactions of methyl vinyl ketone and methacrolein with bisulfite anions lead to the formation of primary bisulfite adducts, using the negative mode electrospray ionization mass spectrometry hyphenated to a reversed-phase liquid chromatography. We also examined in details the kinetics and the mechanisms of the adduct formation to see if the process is relevant for the atmospheric aerosol chemistry.

Materials and methods

Chemicals

The following chemicals were used as purchased: methacrolein (Sigma-Aldrich, 95 %), methyl vinyl ketone (Sigma-Aldrich, 99 %), $Na_2S_2O_5$ (Merck, EMSURE® ACS, Reag. Ph Eur. > 98 %), acetonitrile (Sigma-Aldrich, ChromaSolv, LC/MS grade), glacial acetic acid (Roth, analytical grade) and argon (Multax 99.999 %). For each experiment aqueous solutions of reactants were prepared freshly using Milli-Q water (18.2 MΩ, Milli-Q Advantage System from Merck Millipore). To avoid the contact with the atmospheric oxygen, Milli-Q water was deoxygenated by bubbling a stream of argon over 20 min. The sodium bisulfite solutions were obtained by dissolving $Na_2S_2O_5$ in deoxygenated Milli-Q water:

$$Na_2S_2O_5 + H_2O \rightleftharpoons 2Na^+ + 2HSO_3^- \qquad (3)$$

Under the experimental conditions employed in this work, the species in solutions were predominantly Na^+ and HSO_3^- ions, while the pH of solutions was 4.

The deoxygenated Milli-Q water was also used to prepare the 0.1 % acetic acid solution, as the phase A for the liquid chromatography mass spectrometry analyses.

Measurement methodologies

The reaction of bisulfite ions with methyl vinyl ketone or with methacrolein was run in a 150 cm^3 flask reactor. The aliquots of stock solutions of reactants were mixed with water directly in the flask reactor to start the reaction. The reactor was initially filled with argon to exclude any contact of solutions with oxygen. The reacting solution was magnetically stirred and air-thermostated at 25 ^oC. Samples of the solution (1.5 cm^3) were drawn periodically for measurement of UV spectra. Liquid removed from the reactor was replaced with argon from the attached balloon. High resolution UV spectra were recorded in Hellma Suprasil cuvettes with a 1 cm long optical path using a Jasco V-570 spectrophotometer (200–245 nm spectral range, 0.2 nm bandwidth, 0.5 nm data pitch). Milli-Q water was used as a reference solution. Each reaction run was continued until no change in recorded spectra was observed.

Addition of bisulfite to methacrolein was also studied in a HighTech SF-61 stopped-flow spectrophotometer with a diode-array detector; because the reaction was too fast in the initial period to be reasonably examined in the flask-reactor experiments (see the Results section). The method was suitable for reactions with a time scale of 10 ms to 100 s. Stock solutions of reactants were fed under argon atmosphere to the inlet reservoirs of the spectrophotometer, from which they were injected into the stopped-flow cell made of quartz, which had a 1 cm long optical path. Series of low resolution UV spectra of the reacting solutions were automatically recorded against the time of reaction. The spectrophotometer was calibrated daily against a holmium oxide filter at 0.794 nm bandwidth and data pitch settings. The effective spectral range used was 280–375 nm.

Table 1

Initial concentrations of reactants used in the experiments

Experiments	Methacrolein [mol · dm^{-3}]	Methyl vinyl ketone [mol · dm^{-3}]	HSO_3^- [mol · dm^{-3}]
Flask reactor	$2.806 \cdot 10^{-4}$	$1.762 \cdot 10^{-4}$	$(0.84–1.02) \cdot 10^{-3}$
Stopped-flow	$3.021 \cdot 10^{-2}$		$5.026 \cdot 10^{-2}$

Calculation of concentrations

In the flask-reactor experiments, the concentrations of methyl vinyl ketone and methacrolein were determined directly from the spectra recorded, based on the fact that the absorbance of bisulfite ions was negligible at wavelengths longer than 225 nm at 25 ^{o}C and on the assumption that the products of reaction (2) did not absorb light at this wavelength (Fig. 1):

$$[\mathrm{MVK}]_{time} = A_{time}(225)/(l\varepsilon_{\mathrm{MVK}}(225)) \tag{4}$$

$$[\mathrm{MAC}]_{time} = A_{time}(235)/(l\varepsilon_{\mathrm{MAC}}(235)) \tag{5}$$

where: A is absorbance at given wavelength and time, $\varepsilon_{\mathrm{MVK}}$ and $\varepsilon_{\mathrm{MAC}}$ (mol^{-1} · dm^{3} · cm^{-1}) are the extinction coefficients of methyl vinyl ketone and methacrolein determined from the reference spectra of compounds (Fig. 2), and l (cm) is the length of the optical path.

The concentrations of bisulfite ions could not be measured directly, but were calculated from absorbances at 205 nm, assuming that the adducts produced in reactions (1) and (2) did not absorb light at this wavelength:

$$[\mathrm{HSO}_3^-]_{time} = \frac{A_{time}(205) - [\mathrm{MVK}]_{time}\, l\varepsilon_{\mathrm{MVK}}(205)}{l\varepsilon_{\mathrm{HSO_3}}(205)} \tag{6}$$

where: A are absorbances at given time and wavelength, $\varepsilon_{\mathrm{MVK}}(205)$ and $\varepsilon_{\mathrm{HSO_3}}(205)$ (cm^{-1} · mol^{-1} · dm^{3}) are the extinction coefficients of methyl vinyl ketone and bisulfite ions, respectively (Fig. 4), $l = 1$ cm is the length of the optical path, and $[\mathrm{MVK}]_{time}$ is the concentration of the ketone at given time, determined from the experiment (Fig. 6).

In the stopped-flow experiments, we used more concentrated solutions of reactants and measured the absorbances between 280 and 375 nm. The concentrations of

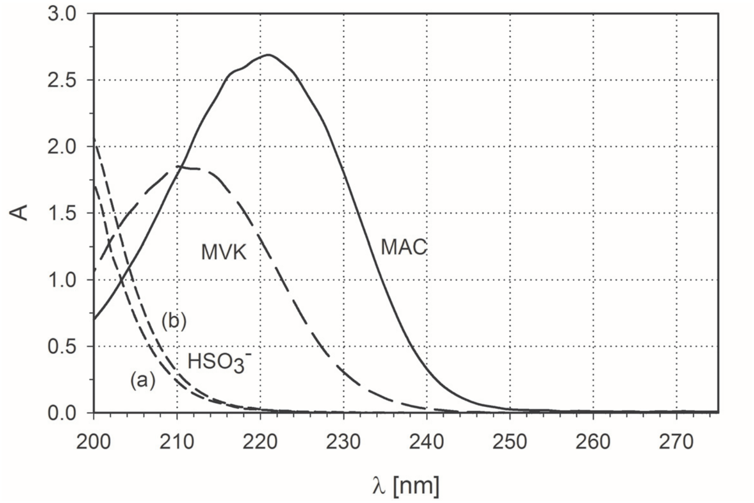


Fig. 1. UV spectra of aqueous solutions of methyl vinyl ketone ($1.762 \cdot 10^{-4}$ M), methacrolein ($2.806 \cdot 10^{-4}$ M) and $NaHSO_3$ (a – $8.498 \cdot 10^{-4}$ M; b – $1.154 \cdot 10^{-3}$ M) at 25 °C

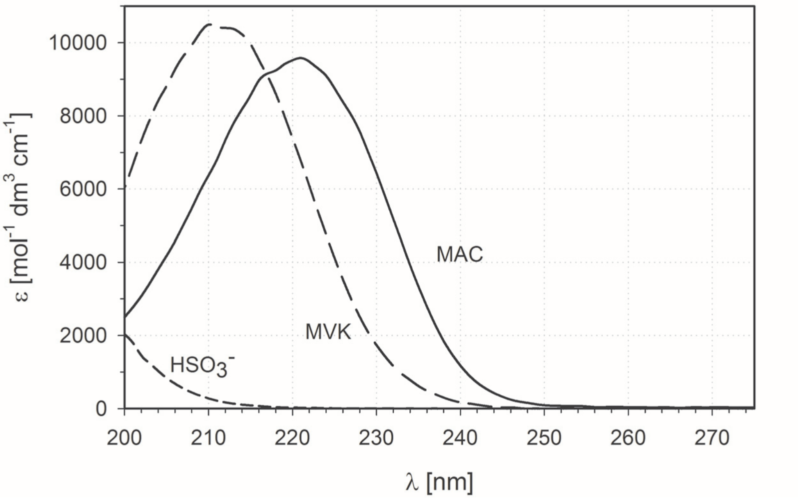


Fig. 2. Extinction coefficients of methacrolein, methyl vinyl ketone and bisulfite ions determined for the milimolar reference solutions using a Jasco V-570 spectrophotometer

methacrolein were determined directly from the spectra recorded, basing on the fact that the absorbance of bisulfite ions was negligible at wavelengths larger than 325 nm at 23 °C and on the assumption that products of reaction (1) did not absorb light at this wavelength (Fig. 3):

$$[\mathrm{MAC}]_{time} = A_{time}(325)/(l\varepsilon_{\mathrm{MAC}}(325)) \tag{7}$$

where: A is absorbance at given wavelength and time, ε_{MAC} ($mol^{-1} \cdot dm^3 \cdot cm^{-1}$) is the extinction coefficients of methacrolein determined from the reference spectrum (Fig. 4) and l (cm) is length of the optical path.

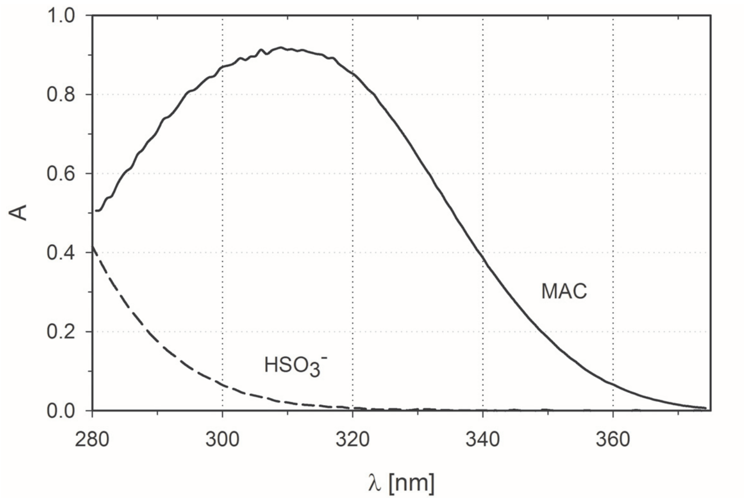


Fig. 3. UV spectra of aqueous solutions of methacrolein ($3.021 \cdot 10^{-2}$ M) and $NaHSO_3$ ($5.260 \cdot 10^{-2}$ M) at 25 °C

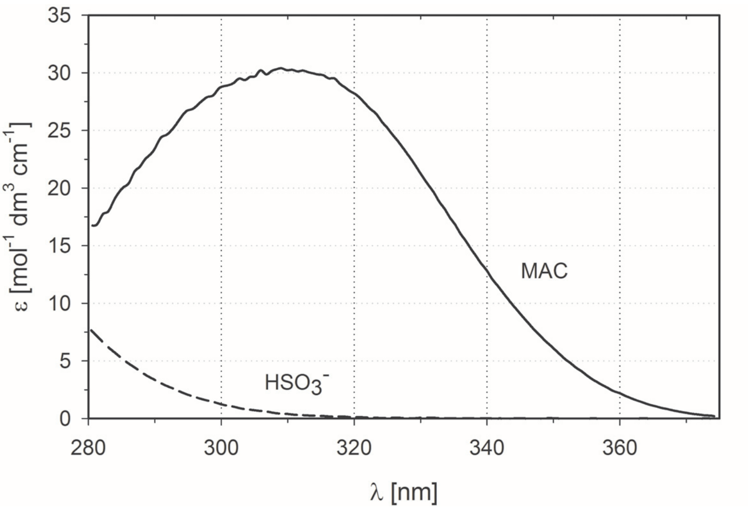


Fig. 4. Extinction coefficients of methacrolein and bisulfite ions at 25 °C determined for concentrated reference solutions using a HiTech SF-61 stopped-flow spectrophotometer

The concentrations of bisulfite ions could not be determined because calculations analogous to equation (6) produced inconsistent results probably due to very low absorbances of bisulfite ions.

Analytical methodologies

The analyses of post-reaction solutions were carried out using a high-performance liquid chromatograph (Agilent Technologies, Agilent 1100) coupled to a triple quadrupole mass spectrometer (Applied Biosystems, API 3000). The chromatographic separation was accomplished using an Atlantis T3 reversed-phase column (Waters, 100 Å, 3 µm, 2.1 mm × 150 mm) and a binary solvent system: 0.1 % acetic acid in water (phase A) – acetonitrile (phase B). The following gradient program was applied: from 0 to 5 min A – 95 %, B – 5 %, than from 5 to 10 min A – 95 % to 5 %, B – 5 % to 95 %, than from 10 to 15 min A – 5 % to 95 %, B – 95 % to 5 %, than from 15 to 20 min A – 95 %, B – 5 %. Before each injection, the aliquots of the reacting solution were diluted 100 times with the deoxygenated Milli-Q water. The flow rate of the mobile phase was kept at the level of 1 cm^3 whereas the injection volume of the sample was $10 \cdot 10^{-6}$ dm^3. The capillary voltage was set in a range of 3–5 kV. The ESI capillary was heated to 150 °C to enhance the process of the ion declustering. Nitrogen was applied as both a nebulizing and a collision gas. The mass spectrometer was equipped with an electrospray ionization source (Applied Biosystem, TurboIonSpray probe). Before each run, the collision energy was ramped and optimized for the selected ion by injecting the mixture of MAC (or MVK) and bisulfite aqueous solution using a direct injection mode. The raw data were processed using the Analyst® software (Applied Biosystems).

Results and discussion

Methyl vinyl ketone

Figure 5 shows absorption spectra recorded in a flask-reaction experiment on addition of bisulfite ions to methyl vinyl ketone. The initial spectrum (time = 0 min)

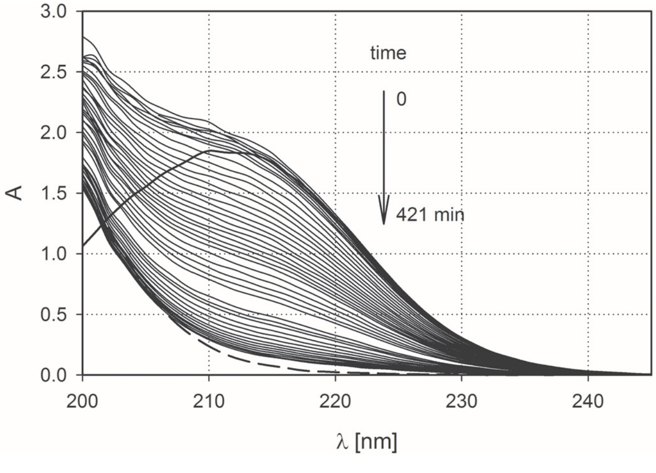


Fig. 5. UV spectra recorded during reaction of methyl vinyl ketone and bisulfite ions in aqueous solutions in a flask--reactor experiment at 25 °C, taken with a Jasco spectrophotometer. Initial concentrations of reactants were: $1.762 \cdot 10^{-4}$ mol · dm^{-3} of methyl vinyl ketone and $8.498 \cdot 10^{-4}$ mol · dm^{-3} of bisulfite (bold solid and dashed lines show respectively the spectra of individual reactants at these concentrations)

was composed from the individual spectra of aqueous solutions of methyl vinyl ketone and sodium bisulfite at concentrations equal to the initial concentrations in the reaction (bold lines in Fig. 5). With the initial concentrations of reactants at the milimolar level, the reaction proceeded fairly steadily and was completed in about 7 hours.

Figure 6 shows the time traces of substrates and reactants in the experiment. Full circles represent the experimental data while lines were obtained by solving a set of ordinary differential eequations (ODE) resulting from the chemical mechanism given in equations (2a) and (2b). Experimental time trace of methyl vinyl ketone was obtained from the cross section of absorption spectra in Fig. 5 at 225 nm. The concentrations of the ketone were calculated using equation (4) while that of bisulfite – using equation (6). Computer simulations were carried out using Mathematica® 9 software.

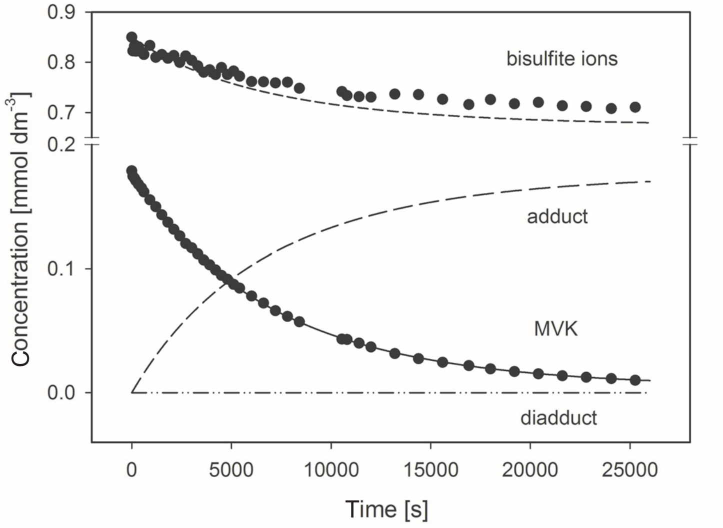


Fig. 6. Time traces of substrates and products in the reaction of methyl vinyl ketone with bisulfite ions at 25 °C – experimental data (circles) from a flask-reactor experiments and computer simulation of the corresponding kinetic model (lines). Initial concentrations of reactants were: $1.762 \cdot 10^{-4}$ mol · dm^{-3} of methyl vinyl ketone and $8.498 \cdot 10^{-4}$ mol · dm^{-3} of bisulfite

Rate constants in the model were adjusted manually by the trial-and guess approach and collected in Table 2.

Table 2

Rate constants for reaction of methyl vinyl ketone with bisulfite ions in aqueous solutions at 25 °C (mechanism 2a and 2b)

k_{MVK1f} [mol^{-1} · dm^3 · s^{-1}]	k_{MVK1b} [s^{-1}]	k_{MVK2} [mol^{-1} · dm^3 · s^{-1}]	$K_{MVK} = k_{MVK1f}/ k_{MVK1b}$ [mol^{-1} · dm^3]
0.18	$3 \cdot 10^{-6}$	$1 \cdot 10^{-6}$	$6 \cdot 10^4$

Uncertainties of the constants were not evaluated because of the insuffiecient number of data.

The experimental and model data agree very well for methyl vinyl ketone and fairly well for bisulfite ions for which the deviation does not exceed 4 %. Thus, the comparison confirms the stoichiometry of reactions (2a) and (2b). The model simulation showed that the dominating product of the reactions was the ketone-bisulfite adduct, while the diadduct was produced in trace quantities, even over very long time.

The observation is in line with the results obtained from the electrospray mass spectrometry analysis of the post-reaction solution. The ESI MS/MS method was selected as the best suited technique for the direct analysis of carbonyl species from the monitored reaction in the aqueous solutions without a prior derivatization [20, 21]. While the positive ESI ion mode was used to monitor the response from methyl vinyl ketone, the reaction products were detected using negative ESI ion mode [22]. Using a direct infusion mode, the first order ESI spectrum acquired for a freshly prepared diluted mixture of MVK and bisulfite aqueous solutions showed a diagnostic peak at *m/z* 151 that dominate the spectrum (Fig. 7). The structure of the ion could be unambiguously assigned to the ketone-bisulfite adduct, as proved by *m/z* 151 → 81 transition recorded in the negative ESI product ion mass spectrum. Interestingly, the *m/z* 151 adduct was also observed in the ESI mass spectrum obtained for the reaction mixture separated using a reversed-phase gradient liquid chromatography. In the extracted ion chromatogram recorded at the *m/z* 151 channel, the corresponding peak emerged at the retention time of 4.31 min. This points to the conclusion that the MVK bisulfite adduct detected at *m/z* 151 is a stable product of the reaction. It is evident that its origin has nothing to do with the electrospray process in the ion source of the mass spectrometer. A careful analysis of the ESI spectrum of the post-reaction samples reveals a weak signal at *m/z* 116 that corresponds to a doubly charged $[M + 2HSO_3^- - 2H]^{2-}$ ion and points to the formation of the bisulfite diadduct. The signal remains weak

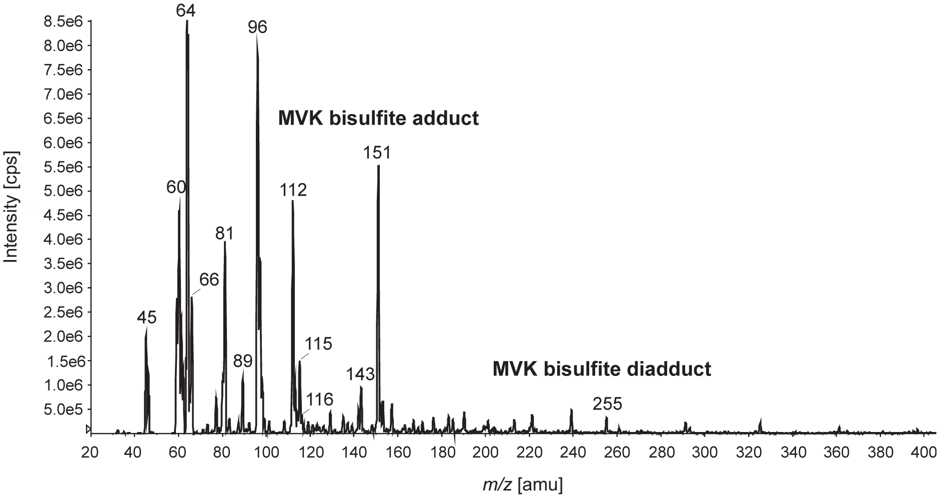


Fig. 7. First order negative electrospray mass spectrum recorded for the reaction mixture of methyl vinyl ketone and bisulfite ion taken a few minutes after mixing. The dominating signals at *m/z* 151 serves as a fingerprint for the formation of the MVK bisulfite adduct

even after long reaction times, indicating that the diadduct is formed in trace quantities. Another diagnostic ion for the MVK bifulfite adduct is the ion at *m/z* 255 in the form of a sodiated cluster $[M + 2HSO_3^- + Na^+]^-$.

Methacrolein

In the first attempt, the addition of bisulfite ions to methacrolein was studied in the same way as for methyl vinyl ketone, but it appeared so fast that the first spectrum that could be recorded showed already a large extent of the reaction (Fig. 8).

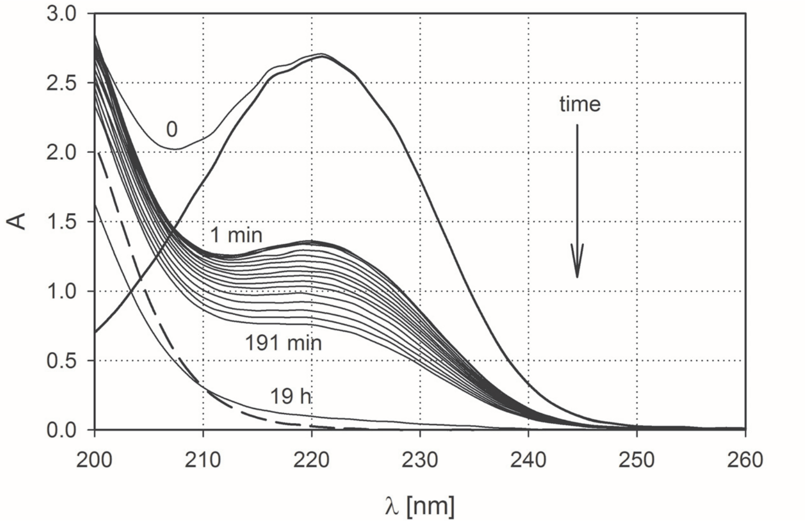


Fig. 8. UV absorption spectra recorded during the reaction of methacrolein and bisulfite ions in aqueous solution taken with a Jasco spectrophotometer in a flask-reactor experiment at 25 °C. Initial concentrations of reactants were: $2.417 \cdot 10^{-4}$ mol · dm^{-3} of methacrolein and $1.140 \cdot 10^{-3}$ mol · dm^{-3} of bisulfite (bold solid and dashed line show respectively the spectra of reactant solutions at these concentrations used to compose the spectrum of reacting solution at time 0)

To obtain complete kinetic observation, we had to use a HighTech SF-61 stopped--flow spectrophotometer with a photodiode array detector. Figure 9 shows the initial sequence of spectra recorded in a stopped-flow experiment at 23 °C. With initial concentrations of reactants at the tenfold milimolar level, the reaction proceeded initially very fast but later significantly slowed down.

Figure 10 shows the time traces of substrates and reactants in the experiment. Full circles represent the experimental data while lines were obtained by stochastic simulation of the chemical mechanism given in equation (1a) and (1b). Experimental trace of methacrolein was obtained automatically from the cross section of the absorption spectra at 325 nm. The concentrations of the aldehyde were calculated using equation (7). Stochastic simulation of the reactions was used because solutions of a corresponding ODE model with Mathematica® software inaccurately approximated

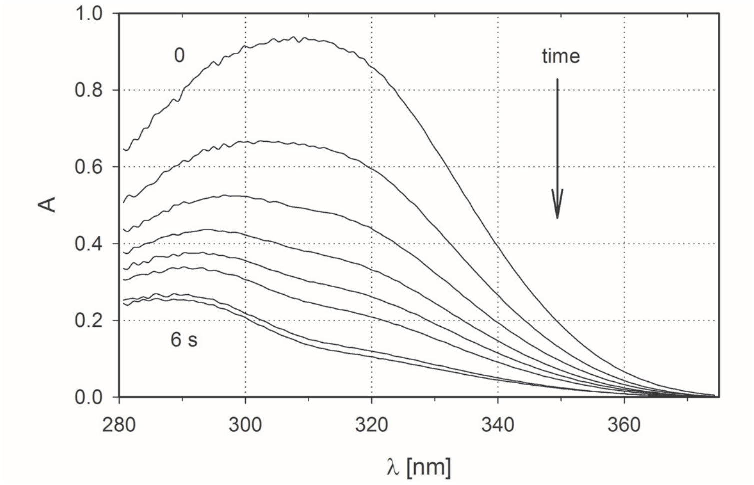


Fig. 9. A sequence of initial UV spectra recorded during reaction of methacrolein and bisulfite ions in aqueous solutions in a stopped-flow experiment at 23 °C. Initial concentrations of reactants were: $3.021 \cdot 10^{-2}$ mol · dm^{-3} of methacrolein and $5.260 \cdot 10^{-2}$ mol · dm^{-3} of bisulfite

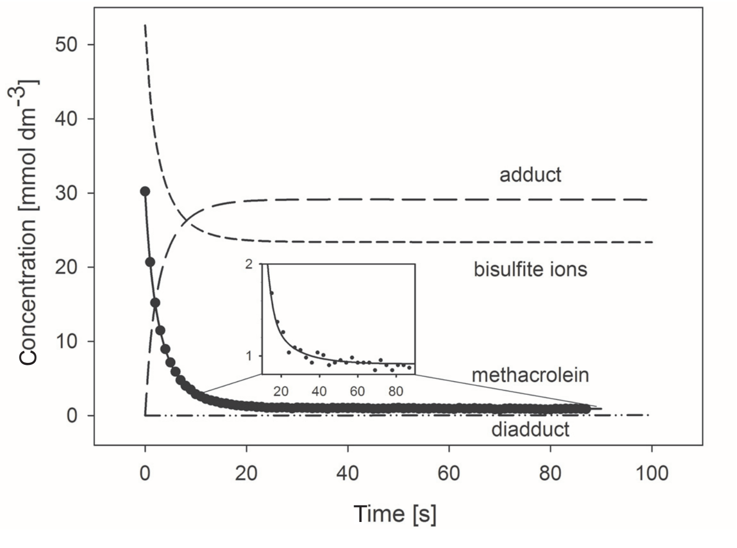


Fig. 10. Time traces of methacrolein in reaction with bisulfite ions at 23 °C – computer simulation of the kinetic model (line) compared well against the experimental data (circles) from a stopped-flow experiment. Initial concentrations of reactants were: $3.021 \cdot 10^{-2}$ mol · dm^{-3} of methyl vinyl ketone and $5.260 \cdot 10^{-2}$ mol · dm^{-3} of bisulfite

the transition from the fast period of the reaction to the slow one. The simulations were carried out using the freely available Chemical Kinetic Simulator software. Rate constants in the model were adjusted manually by the trial-and-guess approach and are collected in Table 3 along with values available from literature.

Table 3

Rate constants for reaction of methacrolein with bisulfite ions in aqueous solutions at 23 °C (mechanism 1a and 1b)

k_{MAC1f} [$mol^{-1} \cdot dm^3 \cdot s^{-1}$]	k_{MAC1b} [s^{-1}]	k_{MAC2} [$mol^{-1} \cdot dm^3 \cdot s^{-1}$]	$K_{MAC} = k_{MAC1f}/ k_{MAC1b}$ [$mol^{-1} \cdot dm^3$]
8 0.65*	$5.8 \cdot 10^{-3}$	$1 \cdot 10^{-3}$	$1.38 \cdot 10^3$

* Determined at 21 °C [19]; Uncertainties of the constants were not evaluated because of the insuffiecient number of data.

The experimental and model data for methacrolein fit quite well. The reaction appeared faster by an order of magnitude than reported in the literature. The model simulation showed that the dominating product of the reactions was the methacrolein--bisulfite adduct, while the diadduct was produced in trace quantities, even over very long time.

The mass spectrometric analysis carried out for the aqueous-phase reaction of methacrolein with bisulfie ions revealed the formation of the corresponding adducts, both mono- and dihydroxysulfonates. Following the reasoning given in the paragraph on the reaction of methyl vinyl ketone with bisulfite ions, the structures of these adducts were determined based on the thorough fragmentation analysis. Using the LC/MS technique we were able to trace down the mono- and diadducts with a good base-line separation. Figure 11 shows an LC trace recorded for a sample of reaction solution with the UV detection at the 256 nm channel. The intense peak at RT 4.47 min corresponds to the MAC bisulfite adduct.

The first order negative electrospray mass spectrum recorded for the 4.47 min peak in the liquid chromatogram corresponds to the MAC bisulfite monoadduct (MW 152).

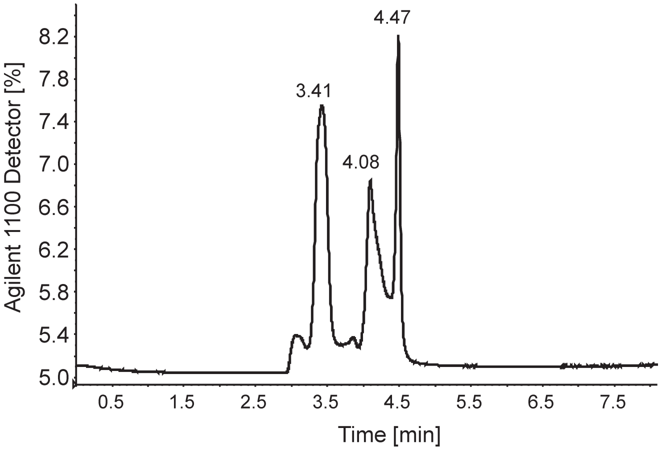


Fig. 11. Liquid chromatogram recorded for a sample from MAC reaction with the UV detection at the 256 nm channel using a tribonded C18 alkyl chain T3 column. The intense peak at RT 4.47 min corresponds to the MAC bisulfite adduct

The spectrum displays the other diagnostic ions: the $[2M - H]^-$ cluster ion at *m/z* 303, where M denotes the mass corresponding to the MAC bisulfite adduct in a neutral form, the $[3M - H]^-$ cluster ion at *m/z* 455 as well as the $[M - MAC]^-$ fragment ion at *m/z* 81.

Conclusions

This work presents for the first time a complete set of rate constants describing the addition of bisulfite ions to methacrolein and methyl vinyl ketone in aqueous solutions at room temperatures. The observations confirm the well-known mechanism of the reaction which consists of a reversible primary addition of bisulfite ion to a carbonyl double bond followed by a slower secondary addition of another bisulfite ion to a C=C double bond in the primary adduct. Generally, the addition to methacrolein was significantly faster than to methyl vinyl ketone. For both compounds, the dominating product was the primary adduct (C_4 alpha-hydroxysulfonate), while the secondary adduct (diadduct, C_4 alpha-hydroxydisulfonate) was produced only in trace quantities, as proved for the first time by the reverse-phase liquid chromatography electrospray tandem mass spectrometric analysis of post-reaction solutions as well as chemical kinetic modelling.

The rate constants for all reactions involved were determined by computer modelling. The only rate constant reported in the literature for the primary addition to methacrolein was more than ten times slower than the one determined. The primary addition of bisulfite ions to methacrolein and methyl vinyl ketone should be considered in atmospheric studies relevant to areas with enhanced presence of sulfur dioxide providing sufficiently high concentrations of bisulfite ions. This regards to the conditions typical of the aerosol particle formation over forested regions with a strong anthropogenic impact.

Further research should include kinetic studies of the bisulfite additions at other temperatures, with particular attention to lower temperatures, as well as product identification studies that would confirm further the mechanism adopted in this work. Moreover, the ambient aerosol studies should include the detection of the bisulfite adducts in field samples.

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PRZYŁĄCZANIE ANIONÓW WODOROSIARCZYNOWYCH DO KETONU METYLOWO-WINYLOWEGO I METAKROLEINY O ZNACZENIU DLA PROCESÓW ATMOSFERYCZNYCH

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Abstrakt: Metakroleina oraz keton metylowo-winylowy są bardzo reaktywnymi zawiązkami karbonylowymi, które odgrywają istotną rolę w procesach atmosferycznych, w tym – w tworzeniu pyłów zwieszonych w powietrzu. Obydwa związki są produktami utleniania izoprenu – węglowodoru emitowanego do atmosfery w ogromnych ilościach. W pracy przedyskutowano mechanizmy chemiczne zaniku metakroleiny oraz ketonu metylowo-winylowego w wyniku addycji anionu wodorosiarczanowego w rozcieńczonych roztworach wodnych, odzwierciedlające procesy zachodzące w kroplach wód atmosferycznych w rejonach o znaczącym stężeniu ditlenku siarki. W pracy pokazano, że reakcje addycji anionu wodorosiarczynowego do badanych związków karbonylowych prowadzą do tworzenia pierwotnych i wtórnych hydroksysulfonianów, które mogą uczestniczyć w tworzeniu aerozoli atmosferycznych. Wyznaczono stałe szybkości wszystkich reakcji w mechanizmie addycji. Pierwotna addycja anionów wodorosiarczynowych do metakroleiny okazała się znacznie szybsza niż do ketonu metylowo-winylowego (stałe szybkości $k_{\mathrm{MAC1f}} = 8$ i $k_{\mathrm{MVK1f}} = 0.18$ $\mathrm{mol^{-1} \cdot dm^{3} \cdot s^{-1}}$ w temperaturach pokojowych). Stała szybkości addycji do cząsteczki metakroleiny była dziesięciokrotnie większa od stałej opublikowanej w literaturze. Analiza kinetyczna i badania produktów reakcji za pomocą spektrometrii mas wykazały, że w przypadku każdego z badanych związków karbonylowych dominującym produktem reakcji był C_4 alfa-hydroksysulfonian (addukt pierwotny), natomiast C_4 hydroksydwusulfonian (addukt wtórny, diaddukt) powstawał w ilościach śladowych. Pierwotna addycja anionów wodorosiarczynowych do metakroleiny i ketonu metylowo-winylowego może mieć znaczenie w konwersji reaktywnych związków karbonylowych w atmosferze i powinna być uwzględniana w badaniach dotyczących rejonów o znaczącej obecności ditlenku siarki, gwarantującej wysokie stężenia anionów wodorosiarczynowych w wodach atmosferycznych.

Słowa kluczowe: procesy atmosferyczne, wtórny aerosol atmosferyczny, stałe szybkości, spektrometria mas z detekcję elektrosprej, LC/MS, izopren, metakroleina, keton metylowo-winylowy, ditlenek siarki, addycja wodorosiaczynu, związki karbonylowe

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POSSIBLE USE OF A WATER RESERVOIR IN CONDITIONS OF AGRICULTURAL ANTHROPOPRESSURE – LAKA DAM RESERVOIR

MOŻLIWOŚCI UŻYTKOWANIA ZBIORNIKA WODNEGO W WARUNKACH ANTROPOPRESJI ROLNICZEJ – ZBIORNIK ZAPOROWY ŁĄKA

Abstract: The paper presents functioning of Laka dam reservoir. It's catchment, drained by the Pszczynka river, is dominated by agriculture. This kind of anthropopressure results in eutrophication of the water environment. The research showed that the reservoir is fed with eutrophicated water. Water fertility increases while flowing through the reservoir. The research included assessment of possible use of the reservoir in such conditions. The reservoir serves flood-control functions and also retains water for industrial plants. Water retained in it cannot be used for consumption. Also, swimming in the reservoir is restricted. It is used for fishing and is regarded as an attractive fishing ground. Increased interest in rest and recreation at the side of the reservoir can be observed. A few water sports centers are operating there. The fact that the banks of the reservoir are managed fosters physical activities. The research shows that multiple-area use of the eutrophic reservoir is possible, but measures aimed to increase water quality are necessary in order ensure comfort and safety for its users.

Keywords: Laka dam reservoir, agricultural anthropopressure, quality of water, water body use

Introduction

Water reservoirs serve multiple utility functions. Among others, they might be used for flood control or retaining water for consumption, industry or agriculture; they could also be used for water sports or plain recreation [1]. Reservoirs are usually multiple-function bodies, unless they were constructed for one particular purpose, *eg* as technological water reservoirs or fishing ponds [2]. Such typically industrial reservoirs are usually located within areas of industrial plants and are not available for people. Other reservoirs are frequently widely available and the way they are used depends on

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multiple factors like location, limnological parameters (including water resources), water quality and accessibility of the shore zone. The most important factor that determines the use of reservoirs is water quality [3]. It determines, inter alia, costs of water treatment for consumption or swimming possibilities. Heavily polluted reservoirs, even those with large water volumes, are poorly managed, which could be seen for example in case of Dzierzno Duze reservoir [4].

Qualitative parameters of water in a given reservoir depend on catchment inflow and processes that occur in the reservoir basin. Quality of water feeding a reservoir is of major importance. The most polluted is water flowing from heavily urbanized and industrialized catchments [5–7]. Municipal-industrial anthropopressure, related to discharge of various waste and downfall from polluted areas, causes water to be not only loaded with suspended matter and overfertilized, but also polluted with trace substances. Also, agricultural anthropopressure has a negative impact on water quality [8–11]. Sapek [12] claims that an inherent element of agriculture is pollution of water with nutrients and its eutrophication (shortage of oxygen, organic load, low transparency, unfavorable color and smell etc.). Additionally, water can be polluted with dangerous micropollutants, *eg* pesticides [13]. Thus, use of water reservoirs which are functioning in agricultural catchments may be seriously restricted.

The specific aim of the paper was to recognize the use of Laka dam reservoir, which functions in an agricultural catchment (Fig. 1). The author assessed water quality in the Pszczynka river, which flows into the reservoir, and also identified and analyzed the forms of use of the reservoir. The paper also had a general aim – to verify common assumptions that agricultural anthropopressure results in deterioration of water quality (including its eutrophication) and thus restricts its use.

Fig. 1. The catchment of Laka dam reservoir. Source: Google Earth

Methods

The first stage of research included collection of materials which characterize the catchment of Laka reservoir. Physiographic papers (publications, reports, expertise, environmental programs), as well as topographic maps and satellite imagery were analyzed. Also, field observations and community research were carried out, mainly regarding agricultural activities.

Stage two included analyses of quality of water which fed the reservoir (water of the Pszczynka river in the zone of its inflow to the reservoir). Water was taken for analyses at a monthly rate in 2011 (12 measuring series). Analyses were carried out in the laboratory of Voivodship Inspectorate of Environmental Protection (VIEP) in Bielsko-Biala. The following parameters were measured: 1) reaction, 2) suspension, 3) dissolved oxygen, 4) biochemical oxygen demand (BOD_5), 5) total organic carbon (TOC), 6) electrical conductivity (EC), 7) sulphates, 8) chlorides, 9) total hardness (TH), 10) ammonium-nitrogen ($N\text{-}NH_4$), 11) total Kjeldahl nitrogen (TKN), 12) nitrate(III)-nitrogen ($N\text{-}NO_2$), 13) nitrate(V)-nitrogen ($N\text{-}NO_3$), 14) total nitrogen (TN), 15) total phosphorus (TP). Methodology of analyses was in accordance with Polish norms and ISO norms. Assessment of water quality was carried out according to respective Polish legal regulations [14–18].

Stage three consisted in recognition and analysis of forms of use of the reservoir. The shore zone was charted and all objects situated near the reservoir which are related to its use were catalogued. Also, field research was carried out to determine forms of use of the reservoir not related to its infrastructure.

Results and discussion

Laka reservoir is situated in the municipality of Pszczyna. It started its operation in 1986 [19]. It was built by damming the valley of the Pszczynka river. With the dam, the water lever is raised in a section about 4 km long – between the dam and the bridge of the road connecting Wisla Wielka and Brzezce villages. Maximum damming level in the reservoir is 250.70 m a.s.l., which makes it possible to retain 12 million m^3 of water (Table 1).

Table 1

Basic parameters of Laka dam reservoir [19]

Water damming level [m a.s.l.]	maximal	250.70
	normal (September–May)	250.35
	normal (June–August)	250.15
	minimal	246.50
Capacity [mln m^3]	total	12.00
	flood (September–May) – included in total	1.35
	flood (June–August) – included in total	2.30
Area [km^2]	at maximal damming level	4.18
	at minimal damming level	0.89
Average depth [m]	at maximal damming level	2.87

Szuster [20] calculated that the reservoir receives average 1.7 m^3/s of water. This is mainly water from the Pszczynka river and its tributaries (major ones including: Debinka, Osiny, Pawlowka, Nieradka, Kanal Branicki, Kanar, Stenclowka). The river flows for about 20 km above the reservoir. Its springs are at about 270 m a.s.l., in the area of the Rybnik Plateau. Several kilometers from the spring, the Pszczynka flows on the area of the Pszczyna Plain [21]. The geological base of both of those regions includes Carboniferous layers, but the surface is dominated by fluvioglacial sands and gravels, loesses, river clays and sands, and silts. Those conditions created brown and podzolic soils, and, in valleys, peat soils.

Physiographic conditions of the catchment of Laka reservoir are favorable for growing agricultural activities. The catchment is an area of 157.92 km^2, of which as much as 121.7 km^2 (77.1 %) is taken by formerly or currently arable land. Forests take 12.7 % of the catchment and urbanized areas – 7.9 % [22]. Farmland is characteristic of the whole area, including the direct catchment of the reservoir (Fig. 1). In the past, it also covered the area which is occupied by the reservoir now. Before flooding the basin of the reservoir with water, 127 ha of arable land, 187 ha of meadows, 95 ha of forested areas and 95 ha or other farmland were bought from owners [19]. After several years, agriculture was restricted also in the backwater zone of the reservoir (above the bridge), and two flood control polders were created.

Results of field observations and community interviews showed that farming activities are the main anthropogenic factor affecting the quality of the water environment in the catchment of the reservoir. Agriculture is related to functioning of villages (*eg* Krzyzowice, Warszowice, Pawlowice, Suszec, Kryry, Studzionka, Mizerow), but wastewater which is produced there is in large part subject to the treatment process [20]. Agriculture has changed in this region in the past several years. Most of small farms were transformed into large ones, which became profitable thanks to specialization. These are livestock farms (pig, poultry, cattle or milk farms), crop farms (grains or rapeseed) or specialized farms (*eg* mushroom growing). What makes a serious threat to water quality is liquid manure from livestock farms, which is poured directly over arable land. On the other hand, specialize crop farms use artificial fertilizers (because of shortage of natural/animal fertilizers), which are washed from soil easily. Periodically, running waters are also contaminated with eutrophic water discharged from fish ponds.

Catchment conditions determine the quality of water entering the reservoir through the the Pszczynka (Table 2). So far, farming anthropopressure has not resulted in contamination with nitrates (which occurs when concentrations of $N\text{-}NO_3$ exceed 11.3 mg/dm^3), which happens in many agricultural regions of Europe as a result of incorrect fertilizing policies [23]. However, limit values of some eutrophication indicators have been exceeded. The average yearly concentration of $N\text{-}NO_3$ in water of the Pszczynka was 3.4 mg/dm^3, and the average yearly concentration of TN was 5.3 mg/dm^3. Eutrophication may occur when the average yearly concentration of $N\text{-}NO_3 > 2.2$ mg/dm^3, and TN > 5 mg/dm^3 [14]. Water of Pszczynka entering the reservoir should be regarded as eutrophic. It was characterized by low concentrations of oxygen (average 5.9 mgO_2/dm^3) and, consequently, excessive concentrations of ammonia and nitrites. High concentrations of dissolved matter were reflected in high values of EC (average

853 μS/cm). According to the legal regulations regarding the environment (Table 2), water under research should not be used for fish farming because of too low contents of oxygen and excessive concentrations of ammonia, nitrites and phosphorus compounds. High concentrations of ammonia and nitrites exclude this water from consumption. Its treatment for consumption is also unjustified (too high values of BOD_5, TOC, EC, $N\text{-}NH_4$, TKN), as it would require expensive, advanced technologies. Values of some parameters of researched water (*eg* reaction, suspension) were equivalent of class one (I), the best class of water quality, but according to the thorough assessment, the quality class was lower than II. These facts show that water of the Pszczynka is contaminated. It flows into the reservoir (still water environment), which may increase eutrophication. Evidence of strong eutrophication of the reservoir was observed periodically during the field research, like algal blooms, unfavorable color, transparency and odor of water. Increased fertility of water from the Pszczynka in Laka reservoir was reported by Niesler and Bielanska-Grajner [24], among others. The authors pointed to unfavorable changes in concentrations and distribution of plankton organisms.

Table 2

Quality of Pszczynka river waters

Parameter	Value range*	Water use for fish farming [15]	Water category for treatment [16]	Water use for drinking [17]	Water quality class [18]
Reaction [pH]	7.05–7.50	yes	A1	yes	I
Suspension [mg/dm^3]	up to 14	yes	A1	#	I
Oxygen [mgO_2/dm^3]	3.4–10.3	no	#	#	I, II and lower class
BOD_5 [mgO_2/dm^3]	2.3–5.3	no/yes**	A1, A2 and A3	#	I and II
TOC [mg/dm^3]	5.6–17.6	#	A2, A3 and out of category	#	I, II and lower class
EC[μS/cm]	656–1095	#	A1, A2, A3 and out of category	yes	I and II
Sulphates [mg/dm^3]	71.8–139.0	#	A1	yes	I
Chlorides [mg/dm^3]	93–219	#	A1	yes	I and II
TH [$mgCaCO_3/dm^3$]	162–222	#	#	yes	I and II
$N\text{-}NH_4$ [mg/dm^3]	0.16–2.76	no	A1, A2, A3 and out of category	no	I, II and lower class
TKN [mg/dm^3]	0.82–3.70	#	A1, A2, A3 and out of category	#	I, II and lower class
$N\text{-}NO_2$ [mg/dm^3]	0.047–0.227	no	#	no	#
$N\text{-}NO_3$ [mg/dm^3]	1.96–6.00	#	A1	yes	I, II and lower class
TN [mg/dm^3]	3.88–7.40	#	#	#	I and II
TP [mg/dm^3]	0.076–0.450	no	#	#	I, II and lower class

Legend: * based on data from VIEP; ** no for salmon family fish, yes for carp family fish; # no restrictions.

Laka reservoir was built for the following purposes [19]:

- to increase low flow on the Pszczynka river (> 1 m^3/s);
- to reduce flood flows (by about 45–46 %);
- to provide water to coal mines of the Rybnik Coal Area;
- to provide water to households and companies from the region of Pszczyna;
- to provide water to the Tychy car factory;
- to provide conditions for rest and recreation for residents of the Silesian conurbation.

The reservoir has not been considered as a part of the water supply system and has been excluded from that function until now. However, it is used in many ways in spite of low quality of its water.

The main function of the reservoir is to provide water to the industry (mainly mining and energy plants). Water is taken by Water Management and Reclamation Enterprise in Jastrzebie Zdroj and distributed for own needs as well as to [25]: Jastrzebie Coal Company (7000 m^3/day), Rybnik Coal Company (7070 m^3/day), Power Engineering Company of Jastrzebie (2900 m^3/day), Laziska Power Station (27600 m^3/day) and other minor recipients (150 m^3/day). For example, the company used 3895478 m^3 of water from the reservoir in 2010 [20]. Water management in the reservoir – water intake with guaranteed flow below the dam (0.3 m^3/s) and flood control functions – generate high fluctuations of water levels. Błażyca [26] reports that in hydrological years 1988–2010 water levels changed between 248.03 m a.s.l. to 250.94 m a.s.l. The highest level was reported during the flood in July 1997 – it exceeded the maximum damming level by 24 cm.

Locally, the reservoir serves flood control functions. Subsequent flood occurrences throughout the time of its functioning showed the need for improvements of its infrastructure (*eg* construction of embankments). After the flood in 1997, additional flood gate was made and flood polders were created in the backwater zone. Currently, a number of additional investments are considered to ensure safety of the reservoir and the city of Pszczyna, which is located below the reservoir.

Laka reservoir is used for fishing. Activities in that regard are administered by the Pszczyna Office 44 of the Polish Angling Association. It has a waterside fishing hotel on the southern bank near the municipality of Wisla Wielka. The administrator is responsible for fish stocking (generally with carp) and registering fishing. In 2010 the reservoir was used by 1390 fishers who caught a total of 11058 kg of fish. The share of the catch was as follows: bream – 40.5 %, pike perch – 23.8 %, carp – 12.8 %, pike – 6 %, ide – 4.8 %, perch – 2.8 %, roach – 2.2 %, tench – 1.8 %, crucian carp – 1.6 %, other – 3.7 % [27]. This distribution was considered favorable because of large share of break and pike perch, which are favored predatory species (only small share of perch is unsatisfactory). Fishing functions of the reservoir, besides recreational-culinary importance, also has an educational aspect – fishing courses are organized there as well as fishing ground cleaning actions.

Laka reservoir plays an important part for recreation. No investments related to this function were planned at the initial stage of its functioning due to the poor quality of its water, resulting from agricultural anthropopressure, which was very strong in the 1980s, and inflow of untreated wastewater. At present, however, the water quality of the reservoir is much better, which results in growth of sports-recreation facilities. Thanks to an agreement between the Regional Water Management Board in Gliwice and Pszczyna Town Hall, 5 campsites were built around the reservoir (camping outside authorized areas is forbidden). Bathing in the reservoir is periodically not recommended – it should be completely avoided in case of algal blooms. On the other hand, activities in water sports, i.e. those using all kinds of sailing equipment, are growing. Within the region of Poreba village, there is a windsurfing center and a branch of Pszczyna Sports Association. They offer rental of sailing equipment and organize sports events. At the bank of the reservoir, near Wisla Wielka, there is a scout hostel, which serves training purposes (swimming, rowing, sailing instructions etc.) for scouts from the Silesian Province and popularizes water sports in many ways. Town's Water Sports Center (a body of the Pszczyna Town Hall) was built on the south-eastern bank of the reservoir, and a beach was created next to it. It enjoys much popularity and contributes to activation of local people. Next to it, there is a private venue "Decha u Lecha", which is the only one at the banks of the reservoir with its own catering facilities. Besides the mentioned venues, walking paths and cycling routes have been arranged near the reservoir (European cycling route EuroVelo 4 runs there).

The range and comfort of use of the reservoir is limited by the quality of its water, and interest in recreation at its banks is growing. Hence, in order to improve water quality, the following measures should be taken: agricultural impact should be reduced by introducing pro-environmental agrotechnology, protecting green zone (free from use of fertilizers) should be established around the reservoir, villages which do not have water treatment plants should be sewered, bottom deposits should be removed from the zone of the Pszczynka inflow to the reservoir, and the bank zone should be cleaned regularly (including removal of excessive vegetation).

Conclusions

1. Agricultural anthropopressure in the catchment of the reservoir has negative impact on the quality of the water environment. Both running and retained water is subject to eutrophication.
2. Contamination of water in the reservoir has no impact on retaining management in case of flood emergency (flood control function of the reservoir is maintained).
3. The eutrophic water body may be a reservoir of water for industry, while its use for consumption is not reasonable, as it would require a costly treatment process.
4. Eutrophication does not exclude fishing functions of the reservoir or using it for practicing water sports. Both of these forms of use may be connected with educational functions.
5. Multiple ways of use of reservoirs which are subject to agricultural anthropopressure are possible; however, steps should be taken in order to improve water quality and, consequently, safety and comfort of users.

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MOŻLIWOŚCI UŻYTKOWANIA ZBIORNIKA WODNEGO W WARUNKACH ANTROPOPRESJI ROLNICZEJ – ZBIORNIK ZAPOROWY ŁĄKA, POŁUDNIOWA POLSKA

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Abstrakt: W pracy przedstawiono funkcjonowanie zaporowego zbiornika Łąka. Na obszarze jego zlewni, odwadnianej przez rzekę Pszczynkę, dominuje działalność rolnicza. Ten rodzaj antropopresji skutkuje eutrofizacją środowiska wodnego. Badania wykazały, że zbiornik jest zasilany wodami eutroficznymi. Żyzność wód wzrasta podczas przepływu przez zbiornik. Rozpoznano możliwości użytkowania zbiornika w takich warunkach. Zbiornik pełni funkcję przeciwpowodziową, a także jest rezerwuarem wód dla zakładów przemysłowych. Zgromadzone w nim wody nie mogą być pobierane z przeznaczeniem na cele konsumpcyjne. Ograniczona jest też możliwość kąpieli. Zbiornik jest użytkowany wędkarsko i stanowi atrakcyjne łowisko. Obserwuje się też ciągły wzrost zainteresowania wypoczynkiem i rekreacją nad zbiornikiem. Działa tu kilka ośrodków sportów wodnych. Zagospodarowanie obrzeży zbiornika sprzyja aktywności fizycznej. Z badań wynika, że wielokierunkowe użytkowanie zbiornika eutroficznego jest możliwe, jednak dla komfortu i bezpieczeństwa użytkowników potrzebne są działania, które poprawią jakość wód.

Słowa kluczowe: zbiornik zaporowy Łąka, antropopresja rolnicza, jakość wód, użytkowanie zbiornika wodnego

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OCCURRENCE OF HEAVY METALS IN RAIN WASTEWATER ON EXAMPLE OF URBAN CATCHMENT IN KIELCE

WYSTĘPOWANIE METALI CIĘŻKICH W ŚCIEKACH DESZCZOWYCH NA PRZYKŁADZIE ZLEWNI MIEJSKIEJ W KIELCACH

Abstract: Rain wastewater flowing from built-up urban areas introduces much pollution into the receiving water environment. The regulation of the Minister of Environment of 24th July 2006 on conditions that have to be met when releasing wastewater into water bodies or soil, and on substances that are particularly hazardous for the aquatic environment only states values of the suspension and those of oil-derived hydrocarbons in rain wastewater delivered to the receiving water. Other hazardous substances, like *eg* heavy metals, are disregarded. Because of the possibility of bioaccumulation, heavy metals can adversely affect the environment, in particular, that of rain wastewater receiving bodies. The paper presents the results of investigations into the level of rain wastewater pollution with heavy metals flowing into the sewer system from the area of the selected catchment, located in the centre of the city of Kielce, which is typically urban in character. For the sake of analysis, four days of spring thaw event were selected, namely those of 22nd Feb. 2010, 23rd Feb. 2010, 24th Feb. 2010, and 14th March 2010. During the passage of thaw water, samples of rain wastewater were collected with an automatic device (sampler) and the concentration of the following heavy metals: Ni, Cu, Cr, Zn, Pb, Cd were determined. The conducted statistical analysis concerning the assessment of the strength of statistical relations between individual pairs of heavy metals in spring thaw event indicated the occurrence of a strong correlation relation only between Ni – Cr, Cu – Cr. The results of investigations were presented in a tabular and graphical form to show the range of variation of concentrations of heavy metals for the observed spring thaw event in the examined Si9 rain water sewer.

Keywords: rain wastewater, spring thaw event, heavy metals

In urbanised areas, atmospheric rainwater poses an increasingly serious problem for the sewer systems because of a continuous growth of city agglomerations. Precipitation water, collected by combined sewer system or rainwater drainage systems, is classified

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as wastewater. The assessment of indicators of wastewater pollution, both with respect to concentration values and factors that influence them, is extremely difficult because of great diversity of those indicators and substantial ranges of values. The data available in the literature [1–6] indicate that the pollution of rain wastewater originates in two sources. First, those are atmospheric pollutants (*eg*: fly-ashes, SO_2, NO_2, CO), which are removed from the atmosphere by precipitation. The other source involves all the pollutants washed away from roads, squares, roofs, parks, *ie* sand, gravel, dust, road salts and de-icing agents, tyre abrasion products, mineral hydrocarbons (oils, lubricants, fuels), animal excrements, leaves and other plant parts, street sweepings, etc.

Heavy metals, found primarily in the airborne particulate matter, are particularly hazardous substances. They are deposited on the ground together with particulate matter, and then they are washed from the catchment and transported, with the rain wastewater, into the wastewater receiving body. Zinc and lead show the highest concentrations in rain wastewater, but in the most heavily polluted runoff portions, copper and chromium, and also cadmium, nickel, arsenic, cobalt and iron are found. The transportation routes are the major sources of heavy metal pollution [1, 7–9].

In rain wastewater, heavy metals occur in the form of dissolved salts, ions or undissolved compounds. A principal source of lead emissions (from 50 % to 98 %) in urbanised areas is municipal transportation. A majority of lead compounds are released with the engine exhaust gas and occur in the form of, *eg* lead halide [10, 11]. All lead compounds are found in high dispersion and they easily undergo sorption onto the surfaces of the atmospheric dust particles. The latter are deposited on hardened surfaces, from where they are washed into the rain wastewater. A high content of lead is also found in snow, which results in elevated, up to a few milligrams per liter, content of this metal in the thaw flow [11, 12]. Gradual decrease in the level of environmental pollution, including rainwater pollution with lead, has been observed due to introducing unleaded petrol. Other elements, the compounds of which are found in substantial amounts in the natural environment, are nickel, cadmium and zinc. The share of zinc in the rain wastewater is the largest and amounts to approx. 60–80 % [11, 13], which results from a wide use of this element, especially in the automotive industry. Compounds of nickel and cobalt are commonly found in nature. Their content in clean air fluctuates around $0.001\ \text{ng} \cdot \text{m}^{-3}$, whereas their elevated levels are related to anthropogenic activities. The main source of cobalt presence in the air are metallurgical industries, especially the manufacture of special-purpose steels, and also glass and ceramics works, where the metal is used, in large quantities, as a dyestuff. The pollution of atmospheric air with nickel is closely related to emissions from metallurgical industries and from combustion of liquid fuels. The concentration of chromium compounds in the air varies considerably. The elevated levels are caused by industries, primarily by non-ferrous metals industry and the manufacture of materials based on cement and limestone. Copper occurrence in the atmosphere results primarily from coal burning and industries (non-ferrous metallurgy). Copper is most frequently bound to dust particles, yet over 90 % of copper found in the atmosphere finds its way to the soil surface and plant surfaces with the atmospheric precipitation. Main sources of rain wastewater pollution with heavy metals in runoffs from roads and motorways are presented in Table 1.

Table 1

Sources of heavy metals in runoffs from roads and motorways according to US EPA report (1995) [2]

Pollutants	Source of pollution
Lead	Leaded petrol and vehicle tyres
Zinc	Vehicle tyres, engine oils and lubricants
Iron	Vehicle body corrosion, metal structure corrosion
Copper	Metallic coatings, fungicides and pesticides
Cadmium	Vehicle tyres, pesticides
Chromium	Chromium coatings on metal parts
Nickel	Diesel oil and petrol, nickel-plated metal surfaces in vehicles, electrical wire connections, asphalt road surfaces

Pollution with heavy metals poses a serious problem for the natural environment. They are indecomposable, and a majority of them, after reaching a certain level of concentration, produces a toxic effect on living organisms [14]. Water pollution with heavy metals is particularly dangerous because in the natural processes of river self-purification, they not only do not undergo biodegradation, but actually due to toxic action on microorganisms, they slow down those processes. Additionally, they can accumulate when combined with organic and inorganic compounds, finally in elevated amounts, they can enter human organisms through a biological food chain causing chronic diseases. It is also necessary to take into account the synergistic effect of some pairs of elements, such as Cu + Cd, Ni + Zn. In view of the above, it seems necessary to lay down legal regulations on admissible concentrations of heavy metals in rain wastewater, which has not been done yet. The Regulation of the Minister of Environment of 2006 [15] defines only admissible concentrations of heavy metals in treated industrial effluent. No attention has been paid to heavy metals in rain wastewater, though in accordance with Appendix 11, they are included in the category of particularly harmful substances causing water pollution, which should be eliminated (List I), or restricted (List II). Additionally, due to high toxicity, even at very low concentrations, lead and all lead compounds (especially the organic ones) are placed on the list of priority substances under the EU Framework Water Directive (2000/60/WE) and also on the sixth place on the list of environmental hazards according to the Environmental Toxicology Section of the Polish Academy of Sciences [16].

Basing on the analysis of investigations conducted by Polish researchers, it can be stated that only few authors studied heavy metal occurrence in rain wastewater. Reports on the amount of those pollutants in runoffs from spring thaw events are rarely found in the literature. In particular, no information is available on the variability in heavy metal concentrations during the passage of the thaw event wave. Analysis of the results from a few available studies [1, 7, 12, 17] indicates accumulation of heavy metals in snow, which poses a serious hazard to receivers, where rain collectors outlets discharge wastewater.

Ranges of concentrations of heavy metals in rain runoffs from urbanised regions, presented in Table 2, provide essential comparative information with respect to investigations conducted for the Kielce area, which is a subject matter of the present paper.

Table 2

Concentrations of heavy metals in rain runoffs from urbanised areas according to domestic authors

Investigations on rain wastewater quality	Ni	Cu	Cr	Zn	Pb	Cd
	$[g \cdot m^{-3}]$					
Krolikowski et al [7]	0.01–0.07	0.05–0.40	0.01–0.10	0.20–5.00	0.10–2.00	0.002–0.008
Garbarczyk [17]	0.02–0.04	0.10–0.20	0.02–0.06	0.30–0.80	0.20–0.40	0.002–0.003
Dabrowski [18]	0.02–0.07	0.02–0.31	0.009–0.097	0.13–1.58	0.03–0.58	0.001–0.008

The data shown in Table 2 indicate that the concentrations of metals in rain wastewater are low. The highest concentrations are observed for zinc and lead (up to 5.0 and 2.0 $g \cdot m^{-3}$, respectively), the lowest are found for cadmium (up to 0.008 $g \cdot m^{-3}$).

The occurrence of heavy metals, especially of lead and zinc, in rain and thaw event wastewater flowing from highly anthropogenically transformed areas was also considered in studies by foreign authors [19]. The average lead content in wastewater from expressways was found to be 0.225 $g \cdot m^{-3}$, whereas the concentration of this element in the sewage from urban areas is, on average, 0.170 $g \cdot m^{-3}$. In Italy, the runoff from urban areas shows the lead content to range 0.006–0.025 $g \cdot m^{-3}$ [20], whereas for residential areas in Austin, Texas this value is 0.016 $g \cdot m^{-3}$, but the runoff from the city roads is approx. 2.5 times more polluted (0.041 $g \cdot m^{-3}$) [21]. As regards nickel, its content in the runoffs from motorways in Germany is 0.024 $g \cdot m^{-3}$, and from roads carrying less heavy traffic, it is 0.010 $g \cdot m^{-3}$ [19]. Similar average values for this element were observed in California: freeways – 0.241 $g \cdot m^{-3}$, roads in uninhabited areas – only 0.075 $g \cdot m^{-3}$ [22].

Large differences in the content of heavy metals in runoffs from anthropogenically transformed areas result from, and are determined by, the occurrence of precipitation, its frequency and intensity. The character of the catchment is also important, therefore concentrations in rain runoffs can differ significantly in catchments that seem similar [23, 24]. It happens so because a majority of the pollutants originate in dry deposition and they are washed off hard surfaces when it rains [25]. Metal concentrations in runoffs from roads depend on the content of particulate matter suspended in water, which is closely related to traffic intensity [26]. Heavy metals show the highest affinity with particles below 0.020 mm in diameter, *ie* those that originate, to the greatest extent, in traffic [27].

Materials and methods

Field research object and its utilities

The catchment located in the central and eastern part of the city, which belongs to Si9 collector was selected for the investigations (Fig. 1). The collector is 1569 m long,

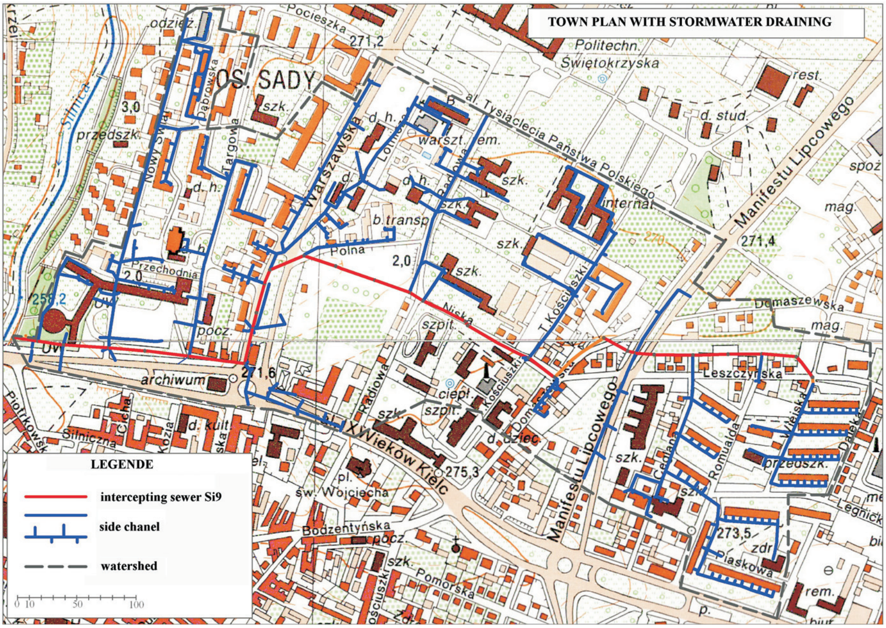

Fig. 1. Catchment of Si9 collector together with a system of lateral sewers [28]

and its diameter varies from 600 mm to 1250 mm. Seventeen lateral sewers, 300–1000 mm in diameter, are connected to it. 32 inspection and connection chambers, and 24 gullies are situated on the collector. On lateral sewers, 119 chambers and 82 gullies are found. The total length of the sewer system is 5583 m. The collector slope varies in different sections from 0.04 % to 3.9 %, whereas for lateral sewers this value amounts up 2.61 %. On average, one gully receives water from an area of 0.585 ha [28]. The vertical datum of the highest point in the catchment area is 271.20 m above sea level, and that of the lowest – 260.0 m above sea level, an average ground surface slope equals 0.71 %. Within the catchment, six types of flow areas were differentiated: roofs (14.3 %), pavements (8.4 %), roadways (17.7 %), car-parks (11.2 %), vegetation (47.2 %) and school yards (1.3 %). In general, hardened surfaces with a high value of flow coefficient constitute 52.83 % of the whole catchment area, which indicates its typically urban character [29]. Rain wastewater from the catchment area under consideration is discharged to the rain wastewater treatment plant located in IX Wiekow Kielc Street.

Description of research apparatus

The research stand was equipped with an automatic device for collecting sewage samples (SAMPLER 6712, which satisfies the requirements of the United States Environmental Protection Agency EPA) and ultrasonic Teledyne ISCO 2150 flow meter. Additionally, in spring and autumn, the rain gauge RG50 by SEBA Hydrometrie

GmbH was installed in the vicinity of the catchment for continuous recording of the rainfall. The rain gauge, which meets the requirements set by the World Meteorological Organisation, was located approx. 3.5 km from the Si9 collector outlet. The sampler was placed in the rain wastewater treatment plant, in a flow splitting chamber, which also contains a horizontal two-chamber sedimentation tank (each chamber 30.0 × 3.6 m) and a coalescence separator ϕ 3.0 m. With a special probe, it automatically collects pre-set amounts of wastewater samples (max. twenty-four 0.5 dm^3 bottles) at pre-set frequency during the passage of thaw water. The flow meter operates by measuring the water column pressure (filling of sewer h) and the mean velocity v in the known sewer cross-section. Those quantities are recorded with AV probe mounted on the adjustable band in Si9 collector, 7 m above the flow splitting chamber. The wastewater flow is calculated as the product of the wetted area of the sewer cross-section and the mean velocity of the wastewater flow. The data are recorded for two rates: every five minutes for wastewater filling sewer $h \leq 5$ cm, and every fifteen seconds for $h > 5$ cm.

The action of both devices mentioned above, *ie* the sampler and flow meter is synchronised over time, which makes it possible to superimpose the data, collected form the instruments with the FLOWLINK program, and to export the data to the Excel spreadsheet, where they can be further analysed and processed. The devices allow recording the following measurements: rainfall, wastewater flow velocity, sewer filling and wastewater flow rate in the sewer measurement cross-section.

Sample collection and laboratory tests

Rain wastewater was collected from 22nd Feb to 14th March 2010 at the time of spring thaw event. The sampler used for wastewater collection was installed approx. 50 m from the sewer outlet into the receiving body. The device was set up in such a way so that it was activated at an instant when the pre-set level of the wastewater in the sewer (5 cm) was exceeded. The wastewater level was recorded by the filling measurement probe, coupled to the device. The level of sampler triggering was adjusted to the year's season, and related to it wastewater sewer filling in rainless weather, which resulted from ground water infiltration. The number of wastewater samples (max. 24–1 bottle for one sample) and the time interval between those (15–40 min) was set separately depending on expected duration of spring thaw event.

The collected unfixed samples were directly transported to the chemical laboratory to determine selected indicators. Tests on rain wastewater concerned, among others, determining the concentration of selected heavy metals, namely Ni, Cu, Cr, Zn, Pb and Cd. Their content was investigated with the method of atomic absorption spectroscopy (AAS) with flame atomisation in accordance with the PN-EN ISO 8288:2002 standard. Prior to determination, the samples were mineralised following the methods described by the EN ISO 15587-1:2002 standard.

Statistical analysis of the results

The values of heavy metal concentrations, obtained separately for each thaw event, were characterised using lower and upper quartiles, median, arithmetic mean, and 5 and

95 percentiles. Because majority of distributions differed from the normal ones, Spearman correlation coefficient was calculated to assess the strength and direction of statistical relations between variables under consideration. The level $p < 0.05$ was accepted as statistically significant. In order to test the zero hypothesis H_0: $r_s = 0$, t statistics with $n - 2$ degrees of freedom was used.

Results and discussion

Spring thaw events recorded from February to March 2010 were characterised by the maximum flow rate from 0.020 to 0.120 $m^3 \cdot s^{-1}$ (Table 3). Each stage was formed under different meteorological and hydrological conditions. The results of investigations into selected heavy metal concentrations in rain wastewater are presented in Table 4.

Table 3

Characteristics of parameters of individual spring thaw events

Item	Date	Number of samples	Parameters of spring thaw event			
			Q_{max} [$m^3 \cdot s^{-1}$]	t_c [min]	t_p [min]	V_c [m^3]
1	22nd Feb	6	0.020	355	200	190.3
2	23rd Feb	12	0.042	515	168	672.3
3	24th Feb	12	0.037	540	220	607.2
4	14th March	22	0.120	765	315	1752.3

The spring thaw event of 22nd Feb. 2010 was caused mainly by the melting of the snow accumulated along the transportation routes. It was the first event of that kind after a period of subzero temperatures. Yet, because of a short duration of positive temperatures and their relatively low values, the flow in the sewer amounted to merely $Q_{max} = 0.020$ $m^3 \cdot s^{-1}$. Due to specific formation of the thaw wave (long melting period from morning till afternoon, *ie* 6–9 hours), the gap between six successive sample collections was set to be 40 minutes. With respect to the total duration of the spring thaw event, which was 355 min (beginning for t = 5 min – Fig. 2a), the measurements covered the period of 200 min.

As regards the spring thaw event of 23rd Feb 2010, positive temperatures during the day were high enough to produce flow in the sewer $Q_{max} = 0.042$ $m^3 \cdot s^{-1}$, twice as much as on 22nd Feb. 2010, for the wave passing at t = 515 min (beginning for *t* = 25 min – Fig. 3a). In order to investigate the variation of heavy metal concentrations more thoroughly, the gap between the collection of successive samples was reduced to 15 min. As a result of disturbances in the running of the program by the sampler, the time of the spring thaw event covered by sample collection was 168 min.

The spring thaw event of 24th Feb. 2010 demonstrated a very similar pattern to that of the previous event (23rd Feb 2010). The flow in the sewer amounted to $Q_{max} = 0.037$

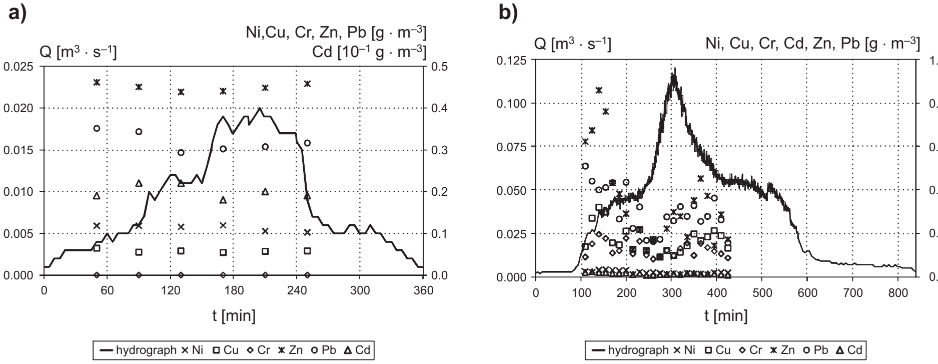

Fig. 2. Variation of heavy metal concentrations in spring thaw events of: a) 22nd Feb. 2010; b) 14th March 2010

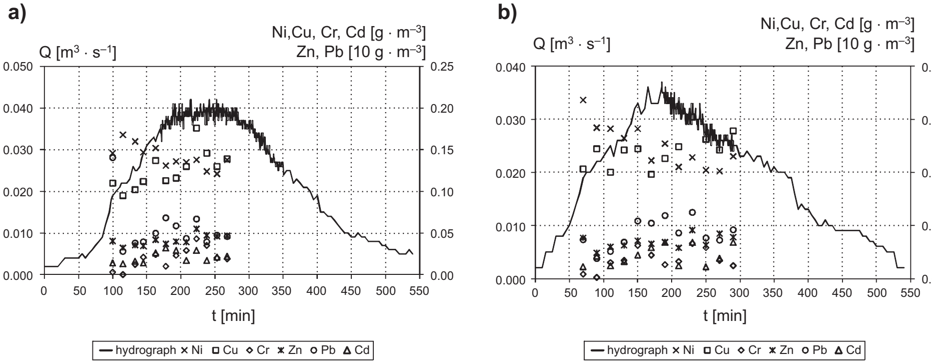

Fig. 3. Variation of heavy metal concentrations in spring thaw events of: a) 23rd Feb. 2010; b) 24th Feb. 2010

$m^3 \cdot s^{-1}$, for the total duration of the wave passage t = 540 min. Within 220 min (between t = 70 min, and t = 290 min – Fig. 3b) 12 rain wastewater samples were collected at 20-min intervals.

The spring thaw event of 14th March 2010 resulted from a heavy snowfall, which started the previous night. Above-zero temperatures during the day caused melting of the accumulated and continuously falling snow and made the flow in the sewer reach the maximum value of 0.120 $m^3 \cdot s^{-1}$, for the event total duration of 765 min. 22 samples were collected at 15-min time intervals (Fig. 2b), thus the overall time of the event covered by sample collection was 315 min.

In the analysed waves, the greatest non-uniformity is observed in the concentrations of Pb, Cu and Zn (Figs 2–4). For two spring thaw events (23rd Feb 2010 and 24th Feb. 2010 – Fig. 3a and b), a clear increasing trend in the concentration of those metals, except for Ni, in the precipitation wastewater can be seen with a growing duration of the wave passage. That is related to a gradual release of pollutants from melting snow piles along the transportation routes. For two remaining waves (Fig. 2a and b), however, the dependence holds in reverse as the concentrations of all metals decrease over time. As

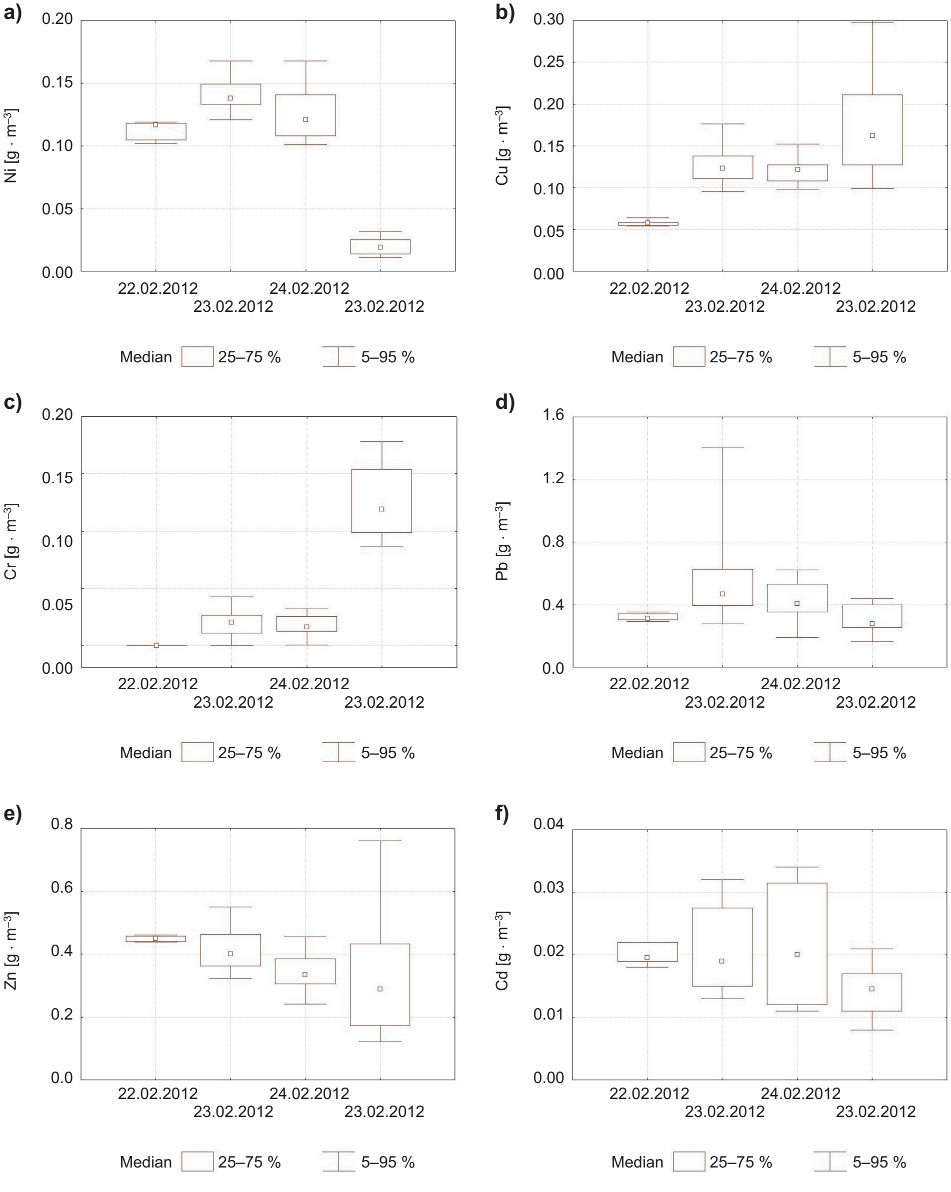

Fig. 4. Box-plot graphs of concentrations of examined metals observed in spring thaw events

regards the event of 22nd Feb. 2010, that is most likely to be connected with relatively short time, at which above-zero temperatures developed, which resulted in low flow in the sewer. Long lasting precipitation of melting snow on 13th–14th March 2010 washed pollutants off the catchment area. No such regularities were observed for heavy rainfall events, where it was difficult to find any repeatable trends in changes [28–30].

The lowest concentrations of Cu, Cr and Pb were observed for the wave of 22nd Feb. 2010. That was definitely related to hydrometeorological conditions in the catchment, which made this spring thaw event the shortest, and the one with smallest flows. In other thaw events, the range of concentration showed irregular characteristics, and it is difficult to decide in which event the wastewater was the most polluted (Fig. 4).

As regards the concentrations of heavy metals, the calculated values of the arithmetic mean usually do not represent the average pollution level of rain wastewater. That is caused by outlier values – most often the maximum ones. It seems justified to use median values and the dominant ones (intervals of the highest cardinality determined by the first and the third quartiles). For instance, characteristic values concerning lead concentrations for the thaw event of 23rd Feb. 2010 are as follows: arithmetic mean 0.554 $g \cdot m^{-3}$, median 0.466 $g \cdot m^{-3}$ with a single outlier, maximum value 1.405 $g \cdot m^{-3}$ (Table 4, Fig. 3a).

Table 4

Statistical measures of analysed concentrations of heavy metals in rain wastewater[a]

Date	Ni	Cu	Cr	Zn	Pb	Cd
	$[g \cdot m^{-3}]$					
22nd Feb.	0.102	0.054	0.000	0.438	0.293	0.018
	0.119	0.064	0.000	0.461	0.351	0.022
	0.116	0.057	0.000	0.449	0.311	0.019
	0.113	0.058	0.000	0.449	0.319	0.020
23rd Feb.	0.121	0.095	0.000	0.323	0.278	0.013
	0.168	0.176	0.043	0.550	1.405	0.032
	0.138	0.123	0.020	0.400	0.466	0.019
	0.141	0.125	0.020	0.412	0.554	0.021
24th Feb.	0.101	0.098	0.001	0.241	0.188	0.011
	0.168	0.152	0.033	0.455	0.622	0.034
	0.121	0.121	0.016	0.334	0.404	0.020
	0.125	0.120	0.017	0.344	0.421	0.021
14th March	0.011	0.099	0.087	0.121	0.163	0.008
	0.032	0.298	0.178	0.760	0.440	0.021
	0.019	0.162	0.119	0.288	0.278	0.014
	0.020	0.174	0.126	0.341	0.305	0.014

* The table presents, in a successive order, the values of: 5 percentile, 95 percentile, median and arithmetic mean for determined heavy metal concentrations in analysed waves.

The statistical analysis performed to assess the strength of statistical relations between all examined pollution indicators in spring thaw events showed the occurrence of pairs of coefficients of moderate Cd – Pb, Cd – Zn, Ni – Cd, Pb – Zn ($r = 0.5$–0.69) and strong Ni – Cr ($r = -0.70$), Cr – Cu ($r = 0.77$) correlation relations. It should be emphasised, however, that all those events were analysed jointly, and correlations might not occur in individual waves, or they can be characterised by different values of correlation coefficient r.

An important feature of rain wastewater that originates in the surface flow is non-uniform discharge of the pollutant load per unit of time. In the literature on the subject, such a release is termed as cumulative effect or shock effect. Because of the reasons described above, it was decided to adopt the concentration expressed with a median (Table 4), which was considered reliable. Additionally, for the last three spring thaw events, samples were not collected throughout the whole time of the events. Therefore, it is difficult to forecast the pattern of concentrations across the whole waves, especially when attempts to adjust the regression (linear, exponential or power) equation produced coefficients of determination R^2 at the level which did not exceed 0.5.

The values of partial loads were estimated on the basis of the following dependence:

$$Ł = s \cdot Q \tag{1}$$

The total mass of pollutants (Table 5), which flowed during a thaw event was determined from the formula:

$$M = \sum_{i=1}^{n} \left(\frac{Ł_i + Ł_{i+1}}{2} \right) \cdot \frac{\Delta t}{1000} \tag{2}$$

On the basis of the table, it can be stated that the qualitative balance of rain wastewater provides relevant information on the magnitude, range and duration of potential effects for the environment. Relying exclusively on concentrations can cause methodology problems, because that does not indicate the real amount of pollutants, in this case heavy metals, introduced into the aquatic environment of the receiving body. The analysis of Table 5 shows that precipitation waters are a source of substantial pollution of surface waters. For instance, the spring thaw event of 14th March 2010, brought 0.505 kg of Zn, 0.487 kg of Pb, 0.283 kg of Cu, 0.209 kg of Cr, and also 0.024 kg of Cd and 0.033 kg of Ni into the receiving body. On the basis of the mass of metals, it can be unequivocally stated that that spring thaw event produced the most pollution, which could not be concluded from the concentration analysis.

Table 5

Mass of heavy metals in rain wastewater in spring thaw events

Date	Ni	Cu	Cr	Zn	Pb	Cd
	[kg]					
22nd Feb.	0.022	0.011	0.000	0.085	0.059	0.004
23rd Feb.	0.093	0.083	0.013	0.269	0.313	0.013
24th Feb.	0.073	0.073	0.010	0.203	0.245	0.012
14th March	0.033	0.284	0.209	0.505	0.487	0.024

To fully understand the scale of the problem, it should be remembered that the paper focused on spring thaw events, which are characterised by much smaller wastewater volume than it is the case with heavy rainfall events. Also, the examined wastewater comes from one rain wastewater catchment and one rain wastewater treatment plant located in IX Wiekow Kielc Street. Presently, about 25 rain wastewater treatment facilities operate in the city area. Majority of them discharge rain wastewater into one receiving water body, *ie* the River Silnica.

Conclusions

1. The mass of heavy metals in thaw wastewater for all four spring thaw events ranges as follows: nickel 0.022–0.093 kg, copper 0.011–0.284 kg, chromium 0.0–0.209 kg, zinc 0.085–0.505 kg, lead 0.059–0.487 kg, cadmium 0.004–0.024 kg.
2. In view of the synergistic action of some pairs of elements, such as Cu – Cd, Ni – Zn, the lack of legal regulations on admissible concentrations of heavy metals in thaw wastewater seems extremely alarming.
3. Concentrations of heavy metals, *ie* Ni, Cu, Cr, Zn, Pb, and Cd in the analysed samples of thaw event wastewater are comparable with typical concentration values for urbanised catchments. Generally, the quality of wastewater under consideration does not differ much from the values reported in the literature, except for Cd and Ni concentrations, which are a number of times higher.
4. For the examined metals, the calculated mean concentrations in most cases do not represent the average pollution level of rain wastewater. That is caused by outlier values – most often the maximum ones. It seems justified to use median values and the dominant ones (intervals of the highest cardinality determined by the first and the third quartiles).
5. The correlation relations between analysed heavy metal concentrations, and their strength characterise only the examined catchment. Whether or not such correlations hold for other catchments needs to be confirmed through performing laboratory tests.

Nomenclature

$Q_{\max}$	maximum flow in the sewer during the passage of an investigated wave $[m^3 \cdot s^{-1}]$
t_c	total time of the analysed spring thaw event [min]
t_p	time of the spring thaw event covered by tests (sample collection) [min]
V_c	total volume of the thaw wave $[m^3]$
Ł	partial load of heavy metals $[g \cdot s^{-1}]$
s	heavy metal concentration at time t_i (median values adopted from Table 2) $[g \cdot m^{-3}]$
Q	wastewater flow rate at time t_i $[m^3 \cdot s^{-1}]$, adopted on the basis of the flow meter readings $[m^3 \cdot s^{-1}]$
M	mass of heavy metals [kg]
$Ł_{i,i+1}$	load of heavy metals for i-th and (i + 1) time step $[g \cdot s^{-1}]$
Δt	time step [s]

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WYSTĘPOWANIE METALI CIĘŻKICH W ŚCIEKACH DESZCZOWYCH NA PRZYKŁADZIE ZLEWNI MIEJSKIEJ W KIELCACH

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Abstrakt: Ścieki deszczowe spływające z zabudowanych obszarów miejskich wprowadzają do środowiska wodnego odbiornika wiele zanieczyszczeń. Rozporządzenie Ministra Środowiska z dnia 24 lipca 2006 r. w sprawie warunków, jakie należy spełnić przy wprowadzaniu ścieków do wód lub do ziemi, oraz w sprawie substancji szczególnie szkodliwych dla środowiska wodnego, definiuje tylko wartości zawiesiny oraz węglowodorów ropopochodnych w ściekach deszczowych odprowadzanych do odbiornika. Pomijane są natomiast inne niebezpieczne substancje, takie jak chociażby metale ciężkie, które ze względu na ich możliwości do bioakumulacji, mogą negatywnie wpływać na środowisko, a w szczególności na odbiorniki ścieków deszczowych. W artykule przedstawiono wyniki badań stanu zanieczyszczenia ścieków deszczowych metalami ciężkimi spływających do systemów kanalizacyjnych z obszaru wybranej zlewni o typowo miejskim charakterze, zlokalizowanej w centrum Kielc. Do analizy wybrano cztery fale roztopowe (22.02.2010 r., 23.02.2010 r., 24.02.2010 r., 14.03.2010 r.), w czasie przejścia, których pobrano za pomocą automatycznego urządzenia (samplera) próby ścieków deszczowych i oznaczono w nich stężenia następujących metali ciężkich: Ni, Cu, Cr, Zn, Pb, Cd. Przeprowadzona analiza statystyczna, której przedmiotem była ocena sił związków statystycznych między poszczególnymi parami metali ciężkich w wezbraniach roztopowych wykazała występowanie silnego związku korelacyjnego wyłącznie pomiędzy Ni – Cr, Cu – Cr. Wyniki badań stężeń metali ciężkich zestawiono tabelarycznie oraz graficznie w celu zobrazowania zakresu zmienności stężeń metali ciężkich dla obserwowanych wezbrań roztopowych w badanym kanale deszczowym Si9.

Słowa kluczowe: ścieki deszczowe, wezbranie roztopowe, metale ciężkie

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SEWAGE SLUDGE AS A SOURCE OF MICROELEMENTS REGARDING FODDER VALUE OF SPRING WHEAT GRAIN

OSADY ŚCIEKOWE JAKO ŹRÓDŁO MIKROELEMENTÓW W ASPEKCIE WARTOŚCI PASZOWEJ ZIARNA PSZENICY JAREJ

Abstract: Agricultural alternative for utilization of municipal sewage sludge from some treatment plants, despite still existent doubts, seems the most optimal solution. The condition, which must be fulfilled for such use of sewage sludge are not only legal restrictions, but also dosage of these materials – well considered and justified by agrotechnology. Therefore, the research aimed at determining whether the use of municipal sludge for fertilization would lead to diversification of the contents of selected microelements in spring wheat grain regarding its fodder value. The experiment was conducted in field conditions on the soil classified to Stagnic Gleysol. Zinc, copper, manganese and iron were assessed after dry mineralization of the material by ICP-AES method. On the basis of obtained results it was stated that application of sewage sludge in moderate doses, in compliance with plant requirement for nutrients did not cause any excessive accumulation of the analysed microelements in wheat grain. However, it should be stated that the problem does not concern only microelement content but also the relationships between them, as has been confirmed on the basis of value of Fe:Mn ratio, which indicated manganese deficiency in the analysed grain, irrespective of the applied fertilization.

Keywords: spring wheat, copper, manganese, iron, zinc

Introduction

Constantly growing amount of municipal sewage generates increasingly larger amounts of sludge forming in the treatment processes. There is no possibility of these materials storage so in Poland management of sewage sludge became an important ecological, technical and economic issue [1]. The problem of sewage sludge manage-

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ment lies in its properties, including chemical composition. Research of Harrison et al [2] identified numerous components, including polycyclic aromatic hydrocarbons, AOX, polychromatic biphenyls, polychlorinated dibenzo-dioxins, nitrosamines, pesticides, antibiotics and many others. Trace elements, which are an integral part of sewage sludge including microelements of fertilizer value, have been relatively well recognized. However, diversification of sewage sludge resulting from their production processes and chemical composition requires watching these elements cycle in the food chain, in the context of their use.

Trace element, including microelement, concentrations in plants result not only from their chemical properties or soil properties, but is conditioned by the amount of the element supplied to the soil with fertilizers and plant abilities for its uptake. Elements are of key importance for plants due to the functions they fulfil in the metabolism as components and activators of enzymes. Therefore, these elements influence the course of many processes occurring in plant, among others the photosynthesis, nitrogen transformations but also synthesis of amino acids [3, 4].

Presented investigations assessed municipal sewage sludge used for fertilization of spring wheat regarding the grain fodder value verified by microelement concentrations.

Material and methods

Investigations were conducted as a field experiment located 10 km west of Krakow (49.9963 N; 19.7011 E). The data from meteorological station were presented in Table 1.

Table 1

Monthly rainfall and average daily temperature at the site during 2005–2007 and long-term mean (1961–1999)

Month	Sum of monthly precipitation [mm]				Monthly average temperature [^{o}C]			
	2005	2006	2007	1961–1999	2005	2006	2007	1961–1999
January	66	58	101	34	–1.2	–2.4	3.2	–3.3
February	33	49	42	32	–4.3	–3.0	1.2	–1.6
March	21	60	61	34	–0.2	0.2	6.0	2.4
April	49	57	15	48	6.8	5.6	8.5	7.9
May	61	52	52	83	11.4	10.9	15.2	13.1
June	41	89	72	97	14.4	15.0	18.4	16.2
July	113	14	71	85	17.6	18.6	19.4	17.5
August	103	104	76	87	15.4	15.6	19.0	16.9
September	27	17	180	54	12.5	13.4	12.4	13.1
October	8	32	48	46	7.1	9.1	7.7	8.3
November	30	21	90	45	3.9	6.3	0.8	3.2
December	47	16	21	41	–0.7	0.9	–1.1	–1.0

The soil from the experimental area was classified as Stagnic Geysol. Table 2 presents selected properties of the soil prior to the experiment outset.

Table 2

Soil characteristics of Stagnic Gleysol from trial location in Czernichow (0–20 cm layer)

Parameter	Unit	Value	Parameter	Unit	Value
pH (KCl)	—	5.6	Fe_{tot}	$mg \cdot kg^{-1}$	2565
Organic matter	$[g \cdot kg^{-1}]$	26.4	Bulk density	$[g \cdot cm^{-3}]$	1.52
N_{tot}		1.59	Solid particle density		2.58
$P_{available}$	$[mg \cdot kg^{-1}]$	71.8	Total porosity	$[cm^3 \cdot cm^{-3}]$	0.41
$K_{available}$		297.5	Sand	$[g \cdot kg^{-1}]$	280
Cu_{tot}		15.8	Silt		580
Zn_{tot}		132.8	Clay		140
Mn_{tot}		2230	Texture	—	Silty loam

The experiment was set up in 2005 by means of randomised blocks method and conducted for three years. The area of each plot was 30 m^2. The experimental design comprised 5 objects in four replications: soil without fertilizers (0), soil fertilized with mineral fertilizers (MF) (110 kgN $\cdot$ ha^{-1}, 58.6 kgP $\cdot$ ha^{-1} and 120 kgK $\cdot$ ha^{-1}), the soil fertilized with pig manure (SM) (14.30 Mg $\cdot$ ha^{-1} fresh mass), soil fertilized with municipal sewage sludge from mechanical-biological treatment plant (SS1) (a dose of 14.15 Mg $\cdot$ ha^{-1} fresh mass) and soil fertilized with municipal sewage sludge from biological treatment plant (SS2) (a dose of 10.26 Mg $\cdot$ ha^{-1} fresh mass). Doses of organic materials were calculated on the basis of their nitrogen concentrations. Nitrogen quantity supplied with organic materials and mineral fertilizers – 110 kg per 1 ha – was the same on all objects. Selected properties of manure and municipal sewage sludge were presented in Table 3.

Table 3

Physical and chemical properties of the organic fertilizers

Parameter	Unit	Pig manure (PM)	Sewage sludge Krzeszowice (SS1)	Sewage sludge Czernichow (SS2)
N_{tot}	$[g \cdot kg^{-1}$ d.m.$]^b$	34.0	26.2	41.6
NH_4^+-N		1.29	0.89	1.62
P_{tot}		12.8	8.2	22.3
K_{tot}		21.8	1.9	1.2
Cu_{tot}	$[mg \cdot kg^{-1}$ d.m.$]^b$	156	103	80
Zn_{tot}		284	1146	950
Mn_{tot}		355	194	112
Fe_{tot}		2158	47779	5391
EC^a	$[mS \cdot cm^{-1}]$	2.89	1.69	0.47
pH (H_2O)	—	8.23	6.23	6.57
Organic matter	$[g \cdot kg^{-1}$ d.m.$]$	831	414	726
Ash	$[g \cdot kg^{-1}$ d.m.$]$	169	586	244
Water content	$[g \cdot kg^{-1}$ f.m.$]^c$	774	703	742

[a] EC – electrical conductivity; [b] data are based on 105 °C dry matter weight; [c] f.m. – fresh matter.

Sewage sludge used for the experiment originated from two municipal treatment plants: mechanical-biological plant in Krzeszowice (SS1) and biological plant in Czernichow (SS2) situated in the Malopolska region. The manure used in the experiment originated from pigs. Before its application manure was stored on the manure plate for 6 months.

In fresh samples of sewage sludge and manure, dry matter content was assessed at 105 °C for 12 h, pH by potentiometer, electrolytic conductivity by conductometer, total nitrogen content after sample mineralization in concentrated sulphuric acid using Kjeldahl's method.

The content of ammonium nitrogen was determined colorimetrically using Nessler reagent. Organic matter content and mineral content were assessed using thermal method in dried and ground material after sample mineralization in a chamber furnace (at 450 °C for 5 h) and ash dissolving in diluted nitric acid (1:2, *v*/*v*). Phosphorus content was assessed colorimetrically on Backman DU640 spectrophotometer and potassium by means of flame photometry (FES) on Philips PU 9100X apparatus. The contents of copper, zinc, manganese and iron were determined by ICP-AES method on JY 238 Ultrace apparatus. The analyses were conducted according to the methodology described in paper by Baran and Turski [5] and work by Krzywy [6].

The field was limed prior to the experiment outset. The measure was conducted according to 1/2 of hydrolytic acidity (962.0 kgCaO $\cdot$ ha^{-1}). The following spring, after basic cultivation measures were conducted, manure and sewage sludge were evenly distributed on the plots area and ploughed. Two weeks later a supplementary fertilization was applied, which was mixed with the soil using cultivator+harrow aggregate. Phosphorus and potassium were supplemented with mineral fertilizers to equal level on all objects (except the control) (phosphorus to 58.6 kgP $\cdot$ ha^{-1} in the form of single superphosphate and potassium to 120.0 kgP $\cdot$ ha^{-1} as 60 % potassium salt). Identical as in the first year doses of components, but exclusively in the form of mineral fertilizers were applied in the second and third year of the research, in order to supplement nitrogen, phosphorus and potassium taken up with wheat yield.

The test plant in the presented experiment was spring wheat, 'Jagna' c.v. Assumed plant density per 1 m^2 was 485. Chemical measures were applied to protect the plantation against weeds (spraying with Puma Universal herbicides manufactured by Bayer CropScience dosed 1 dm^3 $\cdot$ ha^{-1} and Aminopielik Gold manufactured by Makhteshim Agan Agro Poland S.A. dosed 1 dm^3 $\cdot$ ha^{-1}) and against fungal diseases (spraying with Alert 375 S.C. fungicide, manufactured by Du Pont, dosed 1 dm^3 $\cdot$ ha^{-1}).

The length of wheat vegetation period in the individual years depended on the weather conditions. Wheat was harvested at grain full maturity; in the first year of the experiment on 13 August 2005, in the second on 3 August 2006 and in the third on 31 July 2007. In order to determine wheat grain yield in field conditions, the plants were harvested from the area of 4 m^2, separately from each plot. Dry matter (d.m.) content in the grain yield was determined by drying 1000 g of grain at 70 °C to constant weight.

The content of selected microelements was assessed in dried and milled wheat grain after sample dry mineralization in a chamber furnace (at 450 °C for 5 h) and dissolving the residue in diluted nitric acid (1:2, *v*/*v*) [7]. In the prepared solutions analysed element concentrations were assessed using ICP-AES method on JY 238 Ultrace apparatus.

Chemical analysis of the soil and organic materials was conducted in two replications. Analysis of the plant material was conducted in four replications. The precision of the conducted assessments was determined using reference material NCS DC733448 (China National Analysis Center for Iron and Steel). The data concerning the precision and exactness of the conducted assessments were given in Table 4 [8].

Table 4

Amounts (mean ± SD) of metals released for material NCS DC733448, as well as data for analytical precision and accuracy

Metal	The value obtained in current study [mg · kg^{-1} d.m.]	Recommended value [mg · kg^{-1} d.m.]	Precision	Accuracy
Zn	21.0 ± 1.0	20.6 ± 2.2	4.76	1.94
Cu	5.1 ± 0.1	5.2 ± 0.5	1.96	–1.92
Mn	889 ± 6.0	1020 ± 67	0.67	–12.8
Fe	54.5 ± 1.4	58.0 ± 6.0	2.56	–6.03

The effect of applied fertilization on the yield of wheat grain and the content of analysed microelements were assessed by means of the analysis of variance. The significance of differences between arithmetic means were estimated by Duncan test at the significance level $\alpha \leq 0.05$. All statistical computations of the results were made using Statistica 8.0 programme [9].

Results

Yields of spring wheat grain in the first year of the experiment harvested from the objects where pig manure (PM) or municipal sewage sludge (SS1, SS2) were applied were from 370 kg to almost 1000 kg dry mass · ha^{-1} smaller in comparison with the yield on the object where mineral fertilizers (MF) were used (Table 5).

Smaller divergences in the quantities of wheat grain were noted in the second year of the investigations, when the difference between the smallest grain yield obtained after application of pig manure (PM) and the greatest quantity of grain yield obtained after the application of mineral fertilizers, only slightly exceeded 500 kg dry weight per 1 ha area. In the third year of the experiment bigger yields of spring wheat grain were gathered from the objects where pig manure (PM) and municipal sewage sludge (SS1 and SS2) were used in the first year, in comparison with the yields from the object where wheat was fertilized exclusively with mineral fertilizers (MF). No significant differences were observed between grain yield of spring wheat fertilized with sewage sludge from mechanical-biological treatment plant (SS1) and from biological treatment plant (SS2). Only in the third year of the research the difference was significant.

Applied fertilization diversified zinc content in spring wheat grain (Table 5). The lowest amounts of this element were assessed in wheat grain from the object where pig manure (PM) was used in the first year of the research, while wheat grain from the object receiving mineral fertilizers had the highest zinc concentrations.

Table 5

Yield and zinc, copper, manganese and iron content in grain of spring wheat

Treatments		Yield	Zn	Cu	Mn	Fe	Fe:Mn ratio
Fertilizer (F)	Year (Y)	[kg d.m. · ha^{-1}]	[mg · kg^{-1} d.m.]				
0	I	2530	41.15	4.56	30.71	153	4.98
	II	2006	56.77	3.70	35.26	144	4.08
	III	2547	51.33	2.58	17.79	161	9.05
	Mean	2361	49.75	3.61	27.92	153	6.03
MF	I	4308	48.46	4.68	28.14	148	5.26
	II	4979	53.56	4.36	33.38	136	4.07
	III	4305	53.08	3.57	23.41	163	6.96
	Mean	4531	51.70	4.20	28.31	149	5.43
PM	I	3359	34.18	4.11	23.93	155	6.48
	II	4442	49.34	4.19	34.67	163	4.70
	III	5390	45.87	4.76	16.06	134	8.34
	Mean	4397	39.80	4.35	24.89	151	6.51
SS1	I	3936	43.19	4.62	33.77	178	5.27
	II	4834	52.79	4.37	30.54	182	5.96
	III	4700	55.57	4.42	22.50	161	7.38
	Mean	4490	50.52	4.47	28.94	174	6.20
SS2	I	3740	35.14	3.92	27.45	155	5.64
	II	4863	50.42	4.44	31.66	161	5.08
	III	4422	52.36	4.16	14.95	153	10.23
	Mean	4342	45.97	4.17	24.59	156	6.98
LSD $\alpha \leq 0.05$	F	278	1.88	0.26	1.97	7.42	0.69
	Y	216	1.45	0.20	1.53	ns[a]	0.54
	F × Y	482	3.25	0.45	3.41	12.85	1.20

[a] ns – the differences between means are not statistically significant.

The amounts of zinc absorbed with grain yield were higher in the objects where fertilization was applied than on the object without fertilization (0) (Table 6). The analysis of amounts of zinc taken up by spring wheat grain showed them to be lower than in the second and third year in the objects where pig manure (PM) or municipal sewage sludge (SS 1 or SS 2) were used in the first year of the experiment.

Copper concentrations in spring wheat grain (Table 5) in the first year of the research were significantly the smallest in the object where pig manure (PM) and sewage sludge from biological treatment plant (SS2) were used in comparison with the fertilized treatments. In the second year of the investigations, beside wheat grain from the control (0), Cu content in the other fertilizer treatments was on a similar level (4.19–4.44

mg · kg^{-1} d.m.). Bigger differences in this element content were observed in the third year of the research. In the objects where organic materials were applied, Cu content was significantly higher in comparison with the concentration assessed in spring wheat grain fertilized with mineral materials.

Table 6

Zinc, copper, manganese and iron uptake with grain of spring wheat

Treatments		Zn	Cu	Mn	Fe
Fertilizer (F)	Year (Y)	[g · ha^{-1}]			
0	I	104	11.5	78	387
	II	114	7.4	71	289
	III	131	6.6	45	410
	Mean	116	8.5	65	362
MF	I	209	20.2	121	638
	II	267	21.7	166	677
	III	229	15.4	101	702
	Mean	235	19.1	129	672
PM	I	115	13.8	80	521
	II	219	18.6	154	724
	III	247	25.7	87	722
	Mean	194	19.4	107	656
SS1	I	170	18.2	133	701
	II	255	21.1	148	880
	III	261	20.8	106	756
	Mean	229	20.0	129	779
SS2	I	131	14.7	103	580
	II	245	21.6	154	783
	III	232	18.4	66	677
	Mean	203	18.2	108	680
LSD $\alpha \leq 0.05$	F	16	1.61	14	54
	Y	13	1.25	10	42
	F × Y	28	2.79	23	93

[a] ns – the differences between means are not statistically significant.

Amounts of copper absorbed with spring wheat grain yield were diversified not only depending on the applied fertilization but also on the year of research (Table 6). Generally the greatest quantities of copper taken up with spring wheat grain were assessed in the third year of research in the objects where organic materials were applied.

Manganese concentration in spring wheat grain did not reveal any clear changes depending on the applied fertilization (Table 5). Bigger diversification in this element content concerned the years of research. In the two first years of the experiment, irrespective of the applied fertilization, manganese content in grain was on an approximate level. A marked decrease in this element content was registered in wheat grain from the third year of research. It should be emphasized that manganese content in grain decreased most in the objects where pig manure (PM) and sewage sludge (SS1 and SS2) were used.

A decline in manganese content in grain from the third year of research was reflected by the amounts of absorbed Mn, whereas obtained increase in yield, in comparison to the object where mineral fertilizers were applied, did not compensate for this difference (Table 6).

Among the analysed elements iron content in wheat was the most diversified (Table 5). The smallest amounts in the two first years of research were determined in spring wheat grain from the objects where mineral fertilizers were applied (M) (Table 5). In the third year of the experiment the highest content of this element was registered in wheat grain from the object receiving mineral fertilization.

The quantities of iron absorbed with spring wheat grain yield were much higher in the fertilized objects than in the control (Table 6). Generally, in the second and third year of research amounts of iron taken up with grain yield were bigger in the objects where organic materials were applied.

The Fe:Mn ratio is of crucial importance for the assessment of plant supply with iron and manganese. Value of this index in spring wheat grain, irrespective of the applied fertilization indicated manganese deficiency.

Discussion

Numerous results of research on sewage sludge proved their positive influence on biomass production [10, 11]. Considerable dynamics of processes occurring in soil, which depends on sometimes often changing environmental factors strongly modifies the effect of fertilization on growth and development [12], and on chemical composition of plants [13]. Presented investigations demonstrated a lesser effect on wheat grain yield (in the first year of research 2005) of not only sewage sludge but also manure fertilization, *ie* in the objects where in the first year nitrogen was supplied exclusively with these materials. Significantly smaller wheat grain yield in the first year of the experiment in these objects resulted from difficult plant access to nutrients, mainly nitrogen, whose availability from sewage sludge is the function of climatic conditions during the vegetation period, the dose of applied sewage sludge and the value of C:N ratio [14, 15]. Such obvious regress in wheat grain yield observed in the presented investigations, in the first year might have been additionally due to the spring date of sewage sludge application. Spring application of natural materials (manure) or organic waste materials (sewage sludge) on one hand results in a limited availability of nutrients to plants, but on the other significantly reduces the loss of fertilizer components which released from organic compounds and not absorbed by plants may become dispersed in the environment.

Analysis of wheat grain yield over a longer period (3 years) revealed that over time the residual effect of sewage sludge becomes pronounced, which results in increasing wheat grain yield. A positive effect of sewage sludge treatment on Durum wheat biomass yield was demonstrated by Tamrabet et al [16] and Jamil et al [17]. In practice, one should increase the dose of mineral fertilizers applied as top dressing in the spring of the year of sewage sludge application.

The problem of microelement deficiency in human diet and animal feeds occurs in many countries. One of the main reasons is a considerable consumption of cereal products with low content of these elements [18]. Microelement concentrations in plant biomass result from the content of their bioavailable forms in soil. The content and bioavailability of microelements in soil are modified by many factors, among others soil pH, organic matter content, soil sorption capacity, but also by plant ability for their uptake and fertilization [19].

Obtaining high yields for many years involves the necessity of controlling the state of plant supply in microelements and therefore confirming the purposefulness of conducted investigations. According to the data in paper by Møller et al [20], copper content in the analysed grain fulfilled the criteria of animal nutrition. However, while using organic material for plant fertilization one should consider a possible occurrence of periodical deficiencies of this element, which on one hand may result from copper presence in these materials in organic compounds, and on the other from copper binding by humus acids. The hypothesis has been confirmed by the results of research in the object with manure, which contained bigger amounts of copper than the sewage sludge, still the element concentrations in spring wheat grain biomass did not increase significantly. On the basis of obtained results no marked effect of the applied sewage sludge on the content of zinc, manganese or iron in spring wheat grain was assessed in comparison with the plants from the object fertilized with manure. It might have resulted from a relatively poor availability of these elements from sewage sludge. Zinc concentrations in grain were within the range of values regarded as appropriate in respect of animal feeding [20]. Similarly, iron content did not worsen fodder value of the analysed grain [20], which does not mean that the problem of iron deficiency in animals and in people is a rare phenomenon. It is usually caused by a low content of this element available forms in a diet or disturbances in its absorption [18]. Iron uptake by plants may be hindered mainly by the soil pH. A relatively low concentration of this element in grain may have also a physiological background connected with difficulties in its transport from the root system to the aboveground organs, but not with limited uptake from soil. Irrespectively of the applied fertilization, manganese content in the analysed wheat grain, also fulfilled the fodder criteria [20], although with respect of Fe:Mn ratio the values were unfavourable. According to Kabata-Pendias and Pendias [21] value of Fe:Mn ratio is crucial for the balance of enzymatic processes in plants. The values of Fe:Mn ratio obtained in the Author's own studies were markedly higher than 2.5, which indicates manganese deficiency and further may suggest unfavourable effect of iron ions on biochemical processes in plant. The value of Fe:Mn ratio may be also influenced by rainfall which shapes water and air relationships in soil. It was confirmed by the level and monthly distribution of rainfall in 2007.

Conclusion

1. In the first two years of the experiment a lesser influence of fertilization with sewage sludge and manure on spring wheat grain yield was demonstrated in comparison with the yield obtained in the object receiving mineral fertilizers. Bigger yields of spring wheat grain in the objects where organic materials were used for fertilization were obtained in the third year, which resulted from the residual fertilizer effect of the applied materials.

2. The values of Fe:Mn ratio obtained in the Author's own investigations indicate a manganese deficiency in the analysed grain, independently of the applied fertilization.

3. Application of sewage sludge in moderate doses in compliance with plant requirements did not lead to an excessive accumulation of the analysed microelements in wheat grain.

4. Fertilization with sewage sludge, particularly regarding the residual effect is an alternative to natural fertilizers and allows to obtain grain yield due to fodder value estimated by microelement content.

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OSADY ŚCIEKOWE JAKO ŹRÓDŁO MIKROELEMENTÓW W ASPEKCIE WARTOŚCI PASZOWEJ ZIARNA PSZENICY JAREJ

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Abstrakt: Rolnicza alternatywa wykorzystania komunalnych osadów ściekowych z niektórych oczyszczalni, mimo nadal wielu wątpliwości wydaje się najbardziej optymalnym rozwiązaniem. Warunkiem do spełnienia przy takim wykorzystaniu osadów ściekowych są nie tylko obostrzenia umocowane prawnie, ale również przemyślane i uzasadnione agrotechnicznie dawkowanie tych materiałów. Dlatego celem badań było określenie czy wykorzystanie do nawożenia osadów komunalnych spowoduje zróżnicowanie zawartości wybranych mikroelementów w ziarnie pszenicy jarej w aspekcie wartości paszowej. Badania przeprowadzono w warunkach polowych na glebie zaliczonej do Stagnic Gleysol. Cynk, miedź, mangan i żelazo oznaczono po suchej mineralizacji materiału metodą ICP-AES.

Na podstawie uzyskanych wyników stwierdzono, że zastosowanie osadów ściekowych w umiarkowanych dawkach, zgodnych z zapotrzebowaniem roślin na składniki pokarmowe, nie spowodowało nadmiernego nagromadzenia badanych mikroelementów w ziarnie pszenicy. Należy jednak stwierdzić, że problem nie dotyczy tylko zawartości mikroelementów, ale również relacji między nimi, co potwierdzono na podstawie wartości stosunku Fe:Mn, który wskazywał na niedobór manganu w analizowanym ziarnie, niezależnie od zastosowanego nawożenia.

Słowa kluczowe: pszenica jara, miedź, mangan, żelazo, cynk

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EFFICIENCY OF ANTIOXIDATIVE SYSTEM IN SPINACH PLANTS GROWING IN SOIL CONTAMINATED WITH NICKEL

SPRAWNOŚĆ SYSTEMU ANTYOKSYDACYJNEGO ROŚLIN SZPINAKU ROSNĄCYCH W GLEBIE ZANIECZYSZCZONEJ NIKLEM

Abstract: The paper attempted to assess the activity of antioxidative system in cells of spinach plant, 'Matador' c.v., growing in the soil contaminated with Ni. Plant material for analyses was obtained from two pot experiments conducted in 2010 and 2011 in the vegetation hall of the Experimental Station of the University of Agriculture in Krakow. Ni content in the plant aboveground parts was assessed by ICP-ES method, contents of reduced glutathione form by colorimetry and ascorbic acid by titrimetric method.

Nickel content in spinach aboveground parts ranged from 2.00 to 204.5 mg · kg^{-1} d.m. and increased with growing substratum pollution with this element and usually with plant age. The plants contained from 31 to 238 μg GSH · g^{-1} f.m. In the first three objects with 0°, I° and II° degree of substratum pollution according to IUNG classification, this antioxidant contents were higher in comparison with its amount in plants from the control and objects with lower degree of pollution. In the object with the highest nickel dose application, GSH content in plants decreased significantly in comparison with plants from the other objects, while the plants on this object died shortly after germination. Ascorbic acid content in spinach in the both years of experiments ranged from 24.13 to 73.09 mg · 100 g^{-1} f.m. and increased in plants from the successive objects with growing substratum contamination with nickel.

In the first phase of growth spinach plants contained generally much more of GSH and AsA, which indicated much better efficiency of the antioxidative system at the initial period of growth.

Keywords: antioxidative system, glutathione, ascorbic acid, nickel, spinach

Introduction

Glutathione (GSH) is a tripeptide composed of three amino acids residues: glutamic acid, cysteine and glycine. In a plant cell the compound is located in the cytosol,

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chloroplasts, endoplasmatic reticulum, vaculoa and mitochondria [1]. Among the numerous functions of this compound, cell redox regulation and antioxidative buffering are regarded as antioxidative properties [2].

Organic acids, including ascorbic acid (vitamin C) (AsA) also possess antioxidative properties [3]. Ascorbic acid is the most important peroxide scavenger in a plant cell [4, 5]. The compound is present in an apoplast, cytosol, plastids and in vacuola of a plant cell. Ascorbate also occurs in cells in two forms: reduced, as L-ascorbic acid (AsA) and oxidized as monodehydroascorbate radical and monodehydroascorbate (DHA) [6]. Ascorbate is a strong antioxidant reacting with superoxide radical anion, hydrogen peroxide, oxygen singlet and organic peroxide radicals [7]. Antioxidative activity of ascorbate relies also on its participation in the reactions of α-tocopherol and β-carotene regeneration from their radical forms [8, 9] and regulation of the redox potential [10]. Moreover, the compound is the cofactor of many enzymes, particularly those containing the transition metal ions [11]. AsA is an electron donor in the reactions catalysed by ascorbate peroxidase (APX) and stimulates expression of APX coding genes [12]. Ascorbate and glutathione are considered the main antioxidants in plant cells and buffers of oxidoreductive reactions, simultaneously performing key functions in the growth and development, and plant response to stressors in the environment [6, 13]. Ascorbate and glutathione are a part of a complex and complicated antioxidative system in plants [14]. Functioning of these compounds in the antioxidative system complement each other in the Halliwell-Asada ascorbate-glutathione cycle (Fig. 1).

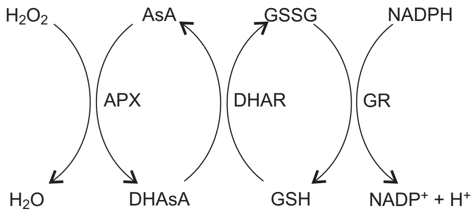

Fig. 1. Scheme of the Halliwell-Asada ascorbate-glutathione cycle [15]

The studies aimed to assess the efficiency of antioxidative system in spinach plants growing in conditions of Ni contaminated substratum on the basis of changes in the content of two basic antioxidants of plant cells: glutathione and ascorbic acid.

Material and methods

Two pot experiments were conducted in 2010 and 2011 in a vegetation hall of the Experimental Station of the University of Agriculture in Krakow, situated in Krakow-Mydlniki. The experimental substratum was obtained from the plots located in the area of the station. Prior to the experiment outset the soil material was analysed and its basic physicochemical properties were determined (Table 1–3).

Table 1

Basic physicochemical properties of soil used in the experiments

pH		Hh	C_{org}	N_{tot}	P_2O_5	K_2O	Water capacity
KCl*	H_2O				acc. to Egner-Riehm		
		$[mmol^{(+)} \cdot kg^{-1}]$	$[g \cdot kg^{-1}]$		$[mg \cdot kg^{-1}]$		[%]
5.75	6.25	9.70	7.50	1.22	157.1	281.6	33.34

* 1 mol · dm^{-3}.

Table 2

Texture of experimental soil

Fraction diameter [mm]	1.0–0.1	0.1–0.05	0.05–0.02	0.02–0.006	0.006–0.002	< 0.002
Share of fraction [%]	45	11	23	13	5	3
Agronomic category	sandy silt loam					

Tabela 3

Total content of macroelements and trace elements in experimental soil

Macroelements	Ca	Mg		K		Na		P
$[g \cdot kg^{-1}]$	1.384	9.913		0.888		0.361		0.443
Trace elements	Fe	Mn	Zn	Cu	Ni	Cr	Pb	Cd
$[mg \cdot kg^{-1}]$	4921	283.3	39.23	14.35	6.637	11.21	0.930	0.266
Degree of pollution [16]	—	—	0^{o}	0^{o}	0^{o}	0^{o}	0^{o}	0^{o}

The experimental substratum was light, slightly acid soil, with average content of organic matter and total nitrogen, high content of available phosphorus and very high content of available potassium. Content of Fe and Pb corresponded to average contents in surface levels of light soils, Mn, Zn, Ni, Cr and Cd contents were little higher than averages, and Cu content was above twice higher than average [16]. Fe, Mn, Zn, Ni, Cr, Pb and Cd contents were lower than limit values for natural these metals content in surface levels of light soils calculated on the basis their geometric means and geometric standard deviations, and higher than limit for Cu [16]. According to degrees of soil pollution elaborated by the Institute of Soil Science and Plant Cultivation (IUNG) [16] heavy metal contents in soil were natural.

The soil was prepared for the experiment by drying in the open air, crushing and sifting. The pots were filled with 5 kg of soil each. A week before the plant sowing uniform basic fertilization was applied to each pot: 1 gN as ammonium nitrate, 0.25 gP as sodium dihydrogen phosphate(V) and 1 gK as potassium chloride. Ni was added to the soil as nickel acetate and applied following the experiment design (Table 4).

Ni supplements corresponded to critical values of the subsequent soil pollution degrees with this metal as suggested by The Institute of Soil Science and Plant Cultivation (IUNG) [16]. Basic fertilization and metal supplements were applied as solutions of pure for analysis salts. Spinach, 'Matador' c.v., was cultivated as a test plant.

Table 4

Scheme of pot experiments

Nickel addition to the substratum	
Degree of contamination acc. to criteria of IUNG [16]	$[\mathrm{mgNi} \cdot \mathrm{kg}^{-1}]$
Control	Natural content
0°	10
I°	30
II°	50
III°	100

Reduced form of glutathione (GSH) was assessed using the method described by Gurie [17] with modifications. Glutathione was extracted from plant tissues using a mixture of ethylenediaminetetraacetic acid and trichloroacetic acid (EDTA-TCA). In order to bring pH solution to the value of *ca* 7.0, K-phosphate buffer with pH = 7.0 was used. The content of reduced glutathione was assessed by spectrophotometer using 5,5-dithiobis-2-nitrobenzoic acid (DTNB) – Ellman reagent in Beckman UV/VIS PU 6400 apparatus. The solution extinction was measured at the wavelength $\lambda = 412$ nm. Glutathione concentration in the plant biomass was calculated on the basis of the values read from the standard curve. Absorbance of the plant homogenate, which absorbed a part of the radiation, was measured as a blind sample.

In order to assess ascorbic acid the plant material was homogenised with 10 % of oxalic acid solution. After sample centrifugation the supernatant was decanted, its volume was assessed and it was titrated with iodine standard in potassium iodide against 1 % starch solution as an index until intensive blue colour appeared. Ascorbic acid content in the test plants was calculated from the amount of iodine in potassium iodide used for titration [18–20].

Nickel content in spinach aboveground parts was assessed using ICP-AES method after wet mineralization in a mixture of HNO_3 and H_2O_2 (6:1, *v*/*v*) in a closed system in a Multiwave 3000 microwave oven (Anton Paar). The solution method was selected for the plants and conducted basing on application instructions of the microwave system manufacturer.

The contents of glutathione, ascorbic acid and nickel were assessed in spinach aboveground parts in three development phases: intensive growth, flowering and seed setting.

Statistical analysis of results was conducted using STATISTICA programme, version 6.0 and Microsoft Excel 2007 calculation sheet. The significance of differences in the analysed chemical compound concentrations in the test plants growing in substrata of various degree of nickel pollution and in successive vegetation phases were assessed using t-Student test at the significance level $\alpha \le 0.05$.

Results and discussion

Nickel concentrations in spinach growing in the control objects in both experiments ranged from 2.00 to 4.96 $\mathrm{mg} \cdot \mathrm{kg}^{-1}$ d.m. (Table 5).

Table 5

Ni contents in biomass of spinach in individual phases of plants development [mg · kg^{-1} d.m.]

Phase of plant development	Nickel addition acc. to degree of substratum contamination				
	control	0^{o}*	I^{o}	II^{o}	III^{o}
			2010		
I phase II phase III phase	2.10^{a} ** 2.00^{a} 3.27^{b}	20.60^{a} 24.83^{b} 26.21^{b}	66.66^{a} 79.59^{b} 77.05^{ab}	128.57^{a} 178.64^{b} 168.22^{ab}	lack of plant material for analyses
			2011		
I phase II phase III phase	4.96^{a} 4.32^{ab} 4.04^{b}	18.16^{a} 20.52^{ab} 24.28^{b}	68.94^{a} 71.32^{a} 82.44^{b}	204.51^{a} 131.48^{b} 158.31^{ab}	lack of plant material for analyses

* Concerns Tables 5–7 and Figs. 1–3: 0^{o}, I^{o}, II^{o}, III^{o} – Nickel additions corresponded to degree of successive substratum contamination acc. to criteria of IUNG [16]; ** concerns Tables 5–7: different letters indicate significant differences depending on nickel additions in relation to control object and objects with lower degree of pollution, at $\alpha \leq 0.05$.

Applied nickel additions caused a significant increase in this element content in spinach aboveground parts. Chen et al [21] reported that Ni uptake by plants in the first place depends on Ni^{2+} ion concentrations in the soil solution. In the presented research in both years of the experiment the first applied supplement caused a 10-fold increase in Ni accumulation in the aboveground parts, whereas the subsequent two admixtures increased its content about 40 and 60-fold, respectively, in comparison with the control. The largest Ni addition, corresponded to III degree of soil pollution caused an inhibition of spinach growth and development (Fig. 2).

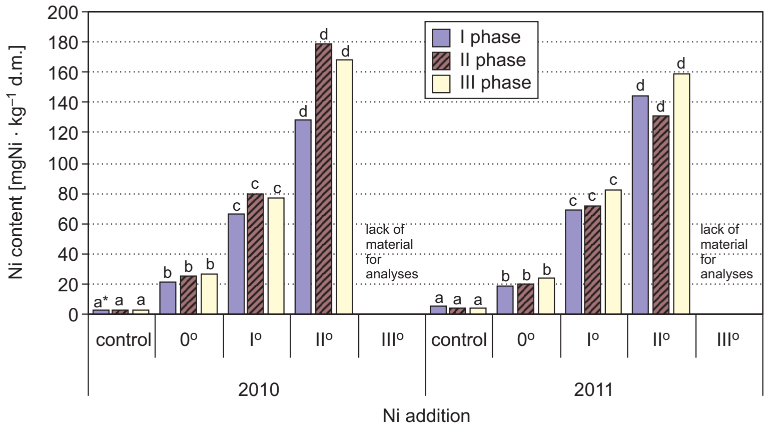

Fig. 2. Ni content in aboveground parts of the spinach in individual phases of development depending on applied metal additions

* Concerns Figs. 2–4: different letters indicate significant differences depending on nickel additions in relation to control object and objects with lower degree of pollution, at $\alpha \leq 0.05$

Kabata-Pendias and Pendias [22] reported that plants growing in the polluted areas may contain even 140 mgNi · kg^{-1} d.m., whereas Molas [23] stated that leaves of cabbage growing in the substratum with between 30 and 90 μmolNi · dm^{-3} contained from 18.21 to 252.54 mgNi · kg^{-1}. Ni contents in spinach aboveground mass harvested from the individual objects in the subsequent development phases generally revealed a growing tendency (Table 5).

Glutathione content in spinach from the objects with Ni addition to the substratum ranged from 41.51 to 140.73 μg · g^{-1} f.m. (Table 6).

Table 6

Glutathione content in biomass of spinach in individual phases of plants development [μg GSH · g^{-1} f.m.]

Phase of plant development	Nickel addition acc. to degree of substratum contamination				
	control	0° *	I°	II°	III°
2010					
I phase	78.92^{a} **	83.23^{a}	91.73^{a}	100.21^{a}	48.72
II phase	64.47^{b}	64.89^{ab}	69.87^{b}	52.64^{b}	—
III phase	31.70^{c}	41.51^{b}	59.10^{c}	73.13^{b}	—
2011					
I phase	87.33^{a}	103.41^{a}	131.04^{a}	140.73^{a}	80.30
II phase	90.76^{a}	111.19^{a}	117.47^{a}	114.09^{b}	—
III phase	59.01^{b}	74.36^{b}	86.81^{b}	108.83^{b}	—

Hawrylak and Szymanska [24] in their research on spinach plant response to various selenium forms assessed glutathione content in plants ranging from 34.58 to 51.10 μg · g^{-1} f.m. In the Authors' own investigations, in the first stage of plant growth and for three first applied nickel supplements, corresponded to 0, I and II degree of soil pollution, glutathione content increased proportionately to Ni concentration in the substratum (Fig. 3).

In the objects with nickel supplement of 100 mg · kg^{-1} of soil (corresponded to III degree of pollution) in both years of the experiment spinach contained markedly less of glutathione than plants from the control or from the other objects with lower degree of soil pollution with this element. Srivastava and Dwivedi [25] registered an increase in GSH content in pea plants under the influence of a small addition of salicylic acid to the substratum, whereas bigger amounts of this compound caused a decline in glutathione content. In the first phase of growth the content of reduced glutathione form in spinach from all objects increased proportionately to the Ni amount in soil corresponded to 0, I and II degree of soil pollution. The greatest nickel addition caused a decrease in the content of reduced glutathione in plant biomass. Spinach plants which contained smaller amounts of glutathione than plants from the control or less polluted objects did not tolerate high concentrations of this element in substratum. In result of high toxicity of this metal, plants from the object with high level of substratum pollution with Ni after germination grew poorly and died. Presence of reduced form of glutathione and

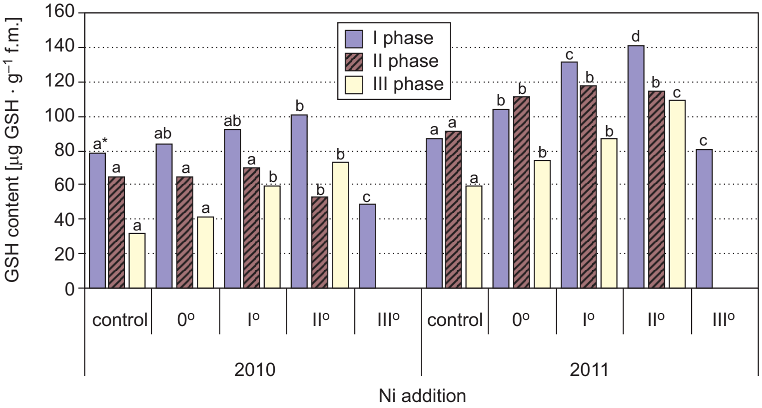

Fig. 3. Glutathione content [µg GSH · g^{-1} f.m.] in aboveground parts of spinach in individual phases of development depending on nickel addition

possibility of regenerating its quota in plant tissue is a condition for tolerance high concentrations of trace elements. Ni present in a plant cell causes numerous disturbances and impairment of all life processes. Each organism has its inherent limit of tolerance to an individual stressor. When the intensity of the stressor is too high and disturbances due to its presence are too serious, the tolerance mechanism fails and the cell dies [26]. Low concentration of reduced glutathione in spinach growing in the substratum with Ni supplement corresponded to III degree of soil pollution might have been connected with high concentration of the element ions in plant cells. Free metal ions, including nickel, impair functions of enzymes, among other glutathione reductase, which is responsible for reduction of oxidized glutathione and therefore for recovering its ability for chelating these ions. Moreover, free ions of toxic elements lead to formation of active oxygen forms which injure and damage lipids, proteins, carbohydrates and nucleic acids, disturbing the correct metabolism of a living cell [27]. Spinach plants growing in the other objects receiving Ni supplement, in the second and third development phase, despite smaller amount of produced biomass than the control plants, tolerated applied additions of this metal. In the 2nd and 3rd phase of growth glutathione content in the plants tolerating this element quantities introduced to the soil and growing in the objects with increasing substratum pollution with Ni, contained greater amounts of GSH. In the 3rd growth phase plants from all objects contained significantly lesser amounts of glutathione in comparison with the analogous objects at earlier stages of growth.

Ascorbic acid (AsA) content in plants from the control in 2010 and 2011 fluctuated from 26.91 to 41.50 mg · 100 g^{-1} f.m. (Table 7).

Kowalska [28] stated that under conditions of diversified liming levels average contents of ascorbic acid in spinach were from 57.62 to 64.36 mg · 100 g^{-1} f.m. On the other hand Ogunlesi et al [29] who assessed ascorbic acid content in spinach by two methods registered between 35.67 and 38.75 mg · 100 g^{-1} f.m. Guri [17] reported mean AsA contents 56.0; 55.4; 56.8 and 55.2 mg · 100 g^{-1} f.m. in plants of four bean varieties, while after their exposure to ozone ascorbic acid declined to: 51.5; 52.0; 51.8 and 51.6 mg · 100 g^{-1} f.m., respectively.

Table 7

Ascorbic acid content in biomass of spinach in individual phases of plants development [mg AsA · 100 g^{-1} f.m.]

Phase of plant development	Nickel addition acc. to degree of substratum contamination				
	control	0° *	I°	II°	III°
	2010				
I phase	41.50^{a} **	44.02^{a}	43.66^{a}	62.05^{a}	72.96
II phase	28.89^{b}	30.58^{b}	35.45^{ab}	39.20^{b}	—
III phase	26.91^{b}	24.13^{b}	32.52^{b}	33.45^{c}	—
	2011				
I phase	40.23^{a}	35.41^{a}	41.31^{a}	47.21^{a}	73.09
II phase	29.56^{b}	29.98^{ab}	28.28^{b}	46.85^{a}	—
III phase	28.16^{b}	28.60^{b}	26.68^{b}	40.39^{a}	—

Contents of ascorbic acid in spinach growing in the substrata with nickel additions ranged from 24.13 to 73.09 mg · 100 g^{-1} f.m. (Table 7). The highest contents of this compound were registered in both years of the experiment in the first phase of plant growth and the concentrations increased proportionately to the quantity of Ni added to the soil. Statistically significant increase in ascorbic acid content in plants in comparison with the control was noted when nickel supplement corresponded to the II and III degree of substratum pollution with this element in all three development phases of the test plants in both years of the experiments (Fig. 4).

Considering AsA content in plants during the vegetation period, the Authors in their own studies found, that spinach contained the greatest amounts of this compound in the 1st growth phase, less in the 2nd, whereas in the 3rd phase its contents were markedly

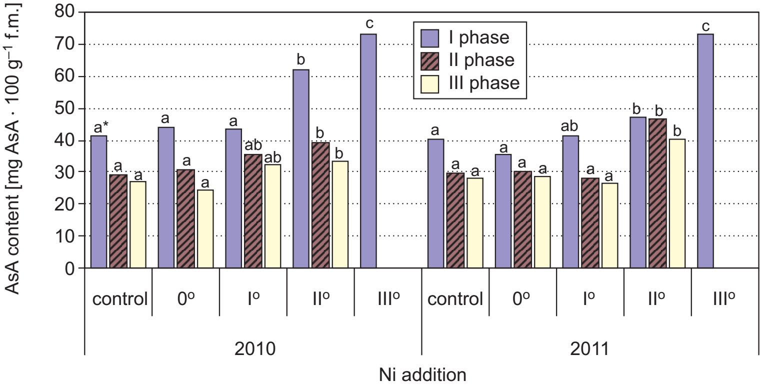

Fig. 4. Ascorbic acid (AsA) content [mg AsA · 100 g^{-1} f.m.] in aboveground parts of spinach in individual phases of development depending on nickel addition

smaller than in the first phase (Table 7). Ascorbic acid content in plants may change under the influence of such factors as: growth intensity, the length of day, the temperature and insolation [30, 31]. Mahan and Wajnura [32] found higher concentrations of ascorbic acid in cotton under conditions of water stress in comparison with plants growing at an adequate irrigation level. Many authors confirm changes in vitamin C content in plants in individual growth phases with a tendency to lowering its level with the plant age [33].

The content of the other investigated cell antioxidant – ascorbic acid in spinach, like glutathione depended on the amount of Ni supplied to the substratum and development phase of the plants. In plants growing in all objects with substrata to various degree contaminated with nickel, increasing content of ascorbic acid was registered along with substratum pollution with this metal. In the objects which received Ni supplement corresponded to the third degree of pollution, concentration of ascorbic acid was the highest, whereas glutathione the lowest in comparison with the control and objects which substratum pollution with this element was lower. A decrease in GSH quota might have been the result of dehydroascorbic acid reduction to ascorbic acid, in which GSH participates. Functions of glutathione and ascorbic acid are interconnected in the Halliwell-Asady cycle [15]. Plants contained the smallest amounts of AsA in the third investigated development phase, which points to better efficiency of antioxidative system in plants in the initial period of their growth and development.

Conclusions

1. Ni doses applied in the experiments caused oxidative stress visible as increased synthesis of antioxidants (GSH and AsA) in spinach plant biomass.
2. Toleration of high Ni concentrations by spinach plants occurs greatly owing to the mechanisms connected with synthesis of antioxidative and buffering compounds (AsA, GSH).
3. During the whole vegetation period and under conditions of stress caused by Ni doses applied to the soil, spinach plants synthetized increased amounts of glutathione, proportionate to Ni content in the soil and plant.
4. Spinach plants growing in Ni contaminated substratum synthetized significantly bigger quantities of ascorbic acid than the control plants in each development phase and in both years of the experiments.
5. The antioxidative system in spinach plant cells acts more efficiently at the initial stage of vegetation, as evidenced by much higher contents of glutathione and ascorbic acid in the first phase of this plant development. At the subsequent stages of plant development successive decrease in antioxidative compounds (GSA and AsA) were observed.

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SPRAWNOŚĆ SYSTEMU ANTYOKSYDACYJNEGO ROŚLIN SZPINAKU ROSNĄCYCH W GLEBIE ZANIECZYSZCZONEJ NIKLEM

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Abstrakt: W pracy podjęto próbę oceny aktywności systemu antyoksydacyjnego komórek roślin szpinaku odmiany 'Matador' rosnących w glebie zanieczyszczonej Ni. Materiał roślinny do analiz pozyskano w dwóch doświadczeniach wazonowych prowadzonych w latach 2010 i 2011 w hali wegetacyjnej stacji doświadczanej

Uniwersytetu Rolniczego w Krakowie. W częściach nadziemnych roślin oznaczono zawartość Ni metodą ICP-ES, zredukowanej formy glutationu metodą kolorymetryczną oraz kwasu askorbinowego metodą miareczkową.

Zawartość niklu w częściach nadziemnych szpinaku wynosiła od 2,00 do 204,5 mg · kg^{-1} s.m. i zwiększała się wraz ze stopniem zanieczyszczenia podłoża tym pierwiastkiem oraz na ogół wraz z wiekiem roślin. Rośliny zawierały od 31 do 238 μg GSH · g^{-1} ś.m. W roślinach z pierwszych trzech obiektów o zanieczyszczeniu podłoża odpowiadającym 0^o, I^o, II^o, według klasyfikacji IUNG, zawartość tego antyoksydantu była większa w porównaniu z zawartością GSH w roślinach z obiektu kontrolnego i obiektów o niższym stopniu zanieczyszczenia. W obiekcie z największym zastosowanym dodatkiem niklu zawartość GSH w roślinach zmniejszyła się istotnie w porównaniu z roślinami z pozostałych obiektów, a rośliny z tego obiektu obumarły niedługo po wschodach. Zawartość kwasu askorbinowego w szpinaku w obydwu latach doświadczeń mieściła się w przedziale od 24,13 do 73,09 mg · 100 · g^{-1} ś.m. i zwiększała się w roślinach z kolejnych obiektów o coraz większym zanieczyszczeniu podłoża niklem.

Rośliny szpinaku w pierwszej fazie wzrostu zawierały na ogół znacznie więcej GSH i AsA, co wskazuje na znacznie wyższą sprawność systemu antyoksydacyjnego roślin w początkowym okresie wzrostu.

Słowa kluczowe: system antyoksydacyjny, glutation, kwas askorbinowy, nikiel, szpinak

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ESTIMATION OF RADIOACTIVITY DOSE RATE ABSORBED WITH INGESTED FOODS

BADANIE WCHŁONIĘTEJ SKUTECZNEJ DAWKI PROMIENIOWANIA OTRZYMANEJ WRAZ ZE SPOŻYWANĄ ŻYWNOŚCIĄ

Abstract: The purpose of the study was to estimate the effective dose of ionising radiation absorbed in consequence of consuming the selected food products for relevant age groups and estimation of the resulting risk. The study was carried out with the use of food products, part of which was produced in the area contaminated with ^{137}Cs released after the Chernobyl Nuclear Power Plant explosion. On the basis of the obtained study results, it can be stated that in consequence of consumption of the selected food products, people may receive increased radiation doses from artificial radioactive isotopes, which are one of the components of the annual effective dose. Taking into consideration other sources of ionising radiation, which are not present in food, one should assume that ^{137}Cs contained in food has a little share in the total radiation dose absorbed by the inhabitants of the studied region.

Keywords: ^{137}Cs, ^{40}K, food, effective weighted dose

Introduction

The potential risk to human health was created by radioactive substances found in the environment. These substances may contain both radionuclides naturally occurring in the environment, and the ones artificially introduced. Globally, the main sources of ionizing radiation in the human environment are natural sources. Approximately 85 % of the annual total radiation dose of any person comes from natural radionuclides of both terrestrial and cosmogenic origin [1–3]. Radioactivity enters the human body through inhalation of radon and thoron gases and their decay products, and by ingestion of the important primordial radionuclides: ^{40}K as well as those from the ^{238}U and ^{232}Th series [3].

Another source of radiation in the environment are artificial radionuclides. Starting from the 40's of the twentieth century, it has been noticed a rapid increase in use of

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radioactive isotopes in various fields of human activity. Initially it was dominated by military applications, which resulted in the release of large amounts of radioactive material into the environment. This was due to a number of nuclear and thermonuclear test explosions.

Radioactive materials had also non-military applications, among them electricity and heat production. Radioactive elements are used in many industrial, medical, and research applications. Frequent use of radioactive materials caused appearance of many problems associated with radiological safety. The disadvantage concerns about the possibility of an uncontrolled penetration of radioactive materials into the environment and subsequently to the human body. Risk exists, despite to the security of today's technology and the development of appropriate procedures for radioactive materials maintenance [4, 5]. These problems concern all the world, because the spread range of the released radioactive materials may include entire countries, continents, and even the Earth [6].

Radionuclides present in the soil are a source of both external and internal exposure to radiation of all living organisms: plants, animals and humans. Radionuclides from soil can be taken up by plants or absorbed by microorganisms, hitting at a later stage to other levels of food chains. Radionuclides in food reach the human body, where their further fate depends on the chemical properties. They can be excreted from the body or accumulated in various organs.

In many regions of the world population living in a specific area primarily feeds on products that have been produced in this area. Radiation exposure per capita is determined by the geological structure of the region, the type of locally produced food, and the presence of anthropogenic sources of radioactive substances. The content of radionuclides in the environment may be affected by the mining industry, combustion deposits, the use of phosphate fertilizers, mine water discharge into water reservoirs. Impact of radioactive substances released as a result, for example, of failure of different devices, leakage of radioactive waste can also be significant.

Due to the significant impact on human health it is necessary to monitor the radiation dose absorbed by the population living in a specific area. An important component of this dose is this part, which is supplied to the body with food. By measuring radionuclide content in food products is possible to evaluate the absorption and thus, the assessment of absorbed dose of ionizing radiation.

Estimation of radiation dose rate received with ingested food meets a number of issues. The diet structure and its seasonal changes as well as foodstuffs sources and age groups distribution in population have to be considered among others. Some of these data could be obtained from institutions which aim is to collect demographic data concerning local population or from laboratories controlling foodstuffs quality. But the necessary information is usually not readily available, even in a part of it.

Radiation dose estimation should be based on a properly designed and carefully conducted experiment. It should involve not only utilization of radioanalytical methods but also the investigation approaches developed by the economical and social sciences. Though such multidisciplinary construction of studies would lead to reliable conclusions, its costs can be very high.

In this paper the simplified approach to the radiation dose estimation, received with the ingested food, is described. It is based on the following assumptions:

1. only the most common foodstuffs were considered in experiment,
2. only the products from the most common in the region foodstuffs suppliers were investigated,
3. only the radionuclides with the relatively big activity concentrations are considered in computations.

Though the results obtained could be burdened by a significant error they should be precise enough to undertake decision whether the detailed, high quality and expensive investigations are required or not.

In order to specify the effective dose received in a date defined period, the radiological protection summarises the effective doses E_z from external exposure during that period and the doses received in consequence of penetration of radioactive nuclides to an organism, during the same period.

Pursuant to the Polish Regulation of the Council of Ministers of 18 January 2005 on Ionizing Radiation Dose Limits [7], the dose limit of ionizing radiation from artificial sources, expressed as the effective dose, amounts to 1 mSv in a calendar year for the total population.

The purpose of the study was to define the effective dose in consequence of consuming the selected food products, for relevant age groups and estimation of the resulting risk. The studies were carried out in the area, which was particularly contaminated with radioactive dust after the Chernobyl disaster. The food products available in the local market were used for measurements.

In order to calculate the effective dose, the obtained results of activity measurements were converted pursuant to the principles described in the standards applicable in Poland. Considering that these standards have been based on the recommendations of international organisations, the conclusions drawn from the studies are of universal nature.

Experimental

The food products for studies were purchased in the shops in Opole (PL). It is a town with 100 thousand inhabitants, in the south-west of Poland. There was a fall of radioactive dust in the Opole region in 1986, in consequence of the nuclear reaction breakdown in Chernobyl (the former Soviet Union) [*eg* 8–10]. One of the elements included in the falling dust was ^{137}Cs, which is still present in considerable quantities in the regional environment.

The study covered the food products, which are relatively popular ingredients of the local diet. These include: potato, rice, barley pearl, white and red kidney bean, oatmeal and sugar. There are products made locally, brought from other regions of Poland and also imported. Also wheat samples from local farms were analysed, as it was the raw material for many other food products.

The products were purchased in large supermarkets, local convenience stores and market places. Different product brands were selected and an approximately 50 g sample was taken from each purchased portion or a packaging. Potato samples were additionally dried to the constant mass at the temperature of 105 °C. The potatoes mass was reduced to approximately 1/4 of the initial value. The obtained materials were mixed and radioactivity assessment was carried out with an approximately 0.5 dm^3 sample.

The measurements of activity concentrations of gamma radionuclides 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 (Czech Metrological Institute, Prague, CZ) which covers an energy range from 59.54 keV to 1836.06 keV. Geometry of calibration source was Marinelli (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. Geometry of samples container was Marinelli, 450 cm^3. Measuring process and analysis of spectra were computer controlled with use of the software GENIE 2000. The radiation spectrum was recorded day and night.

Results and discussion

In the foodstuff samples the activity concentrations of gamma radioactive nuclides were determined. The number of radionuclides detected was different in each sample. In the gamma radiation spectrum the energies characteristic for, among others, ^{228}Ac, ^{211}Bi, ^{212}Pb, ^{235}U were detected but activity concentrations of them were lower than the Minimum Detectable Activity (MDA).

The measurements showed that that the most active in food samples were ^{40}K and ^{137}Cs. The measurement uncertainty, estimated by the GENIE 2000 software, was limited in the range 10–50 % for ^{137}Cs and 2–5 % for ^{40}K. Further computations focused on the results of activity concentration measurements of these radionuclides.

Due to the importance of potassium for living organisms' physiology, one should expect that the content of ^{40}K in food products depends mainly on the type of the used vegetable material. The content of ^{137}Cs depends mainly on the local soil contamination with this radionuclide [11–13].

Table 1 presents the activity values of ^{40}K and ^{137}Cs for the foods studied in the present work and, for comparison, some activities measurements results found in the literature.

The results of measurements of ^{40}K and ^{137}Cs activity presented in Table 1 in the selected food products indicate the presence of anthropogenic isotope ^{137}Cs in potato, wheat, barley pearl and sugar. The presence of the isotope in the tested products signifies contamination of environment with ^{137}Cs and transfer of the isotope from soil to edible plants and then to food products.

It should be noted that radionuclides activity in potatoes refers to the dry mass of the sample. In the drying process, the samples decreased to approximately 25 % of the initial mass. That is why it can be assumed that the specific activity of fresh, not dried potatoes is approximately 4 times lower than the activity of the dry mass.

Table 1

Results of determination of ^{40}K and ^{137}Cs activity concentrations obtained in the present work and described in the literature

Samples	^{40}K	^{137}Cs	References
	[Bq/kg d.m.]		
Potato	633.9	0.6	Present work
Wheat	117.8	1.1	Present work
Rice	22.8	—	Present work
Barley pearl	107.7	0.3	Present work
White kidney bean	496.5	—	Present work
Red kidney bean	428.0	—	Present work
Oatmeal	118.4	—	Present work
Sugar	4.58	0.18	Present work
Potato	166.7	—	[14]
Wheat	150.8	—	[14]
Rice	70.3	—	[14]
Soy	311	< 0.13	[15]
Bean	434	< 0.29	[15]
Wheat	96	< 0.07	[15]
Rice	14.7	< 0.04	[15]
Wheat no. 1	127.9	0.26	[16]
Wheat no. 2	145.1	0.15	[16]

Data in Table 1 show much larger activities of the natural isotope ^{40}K than activities of ^{137}Cs. The activities measured during our experiments are similar to the values referred to in literature [14–16]. Due to the abundance of ^{40}K in potassium amounting to 0.0118 %, activity of this isotope is directly related to the content of potassium in the analysed material. That is why assessment of ^{40}K activity can be performed on the basis of the results of chemical analysis of potassium content in a sample.

The obtained measurement results, as well as the information published in relevant legal acts binding in Poland, were used for the assessment of risk related to the consumption of foods. The method of calculating internal exposure doses presented in the regulation is based on the following international regulations:

– basic international standards of protection from ionizing radiation and security of radiation sources (developed under the auspices of UN, IAEA, International Labour Organization),

– basic security standards of health protection from ionizing radiation for employees and total population (EU Council Directive 96/29/EURATOM) [17].

The indicators included in the Polish Regulation [7], were applied in order to calculate the annual dose of internal exposure, caused by the consumption of selected foods. The loading effective dose *E*, being a result of a nuclide penetrating through the digestive system, was calculated from the formula 1:

$$E = e(g)A \tag{1}$$

where: $e(g)$ is conversion factor for persons in the age group g expressed in Sv/Bq, and A is the activity of a radionuclide, which penetrated into the organism through the digestive and respiratory systems, expressed in Bq.

Together with the consumed foods, our organism is penetrated not only by the natural radioactive isotopes (especially ^{40}K), but also by the radioactive ^{137}Cs, which is accumulated in all soft tissues, and consequently removed from the organism.

The committed effective doses of ^{137}Cs and ^{40}K, included in table 4 of the Regulation for the total population, related to the penetration of a nuclide with the activity concentration of 1 Bq, are shown in Table 2.

Table 2

Values of the committed effective doses of ^{137}Cs and ^{40}K in different age groups g, related to penetration of a nuclide with the activity concentration of 1 Bq [7]

$e(g)$ [Sv/Bq]	$g \le 1$ year	$g > 1$ year	$g = 2–7$ years	$g = 7–12$ years	$g = 12–17$ years	$g > 17$ years
^{137}Cs	$2.1 \cdot 10^{-8}$	$1.2 \cdot 10^{-8}$	$9.6 \cdot 10^{-9}$	$1.0 \cdot 10^{-8}$	$1.3 \cdot 10^{-8}$	$1.3 \cdot 10^{-8}$
^{40}K	$6.2 \cdot 10^{-8}$	$4.2 \cdot 10^{-8}$	$2.1 \cdot 10^{-8}$	$1.3 \cdot 10^{-8}$	$7.6 \cdot 10^{-9}$	$6.2 \cdot 10^{-9}$

Tables 3 and 4 present the calculated effective doses received in consequence of absorbing isotopes ^{137}Cs and ^{40}K with the consumed food for the persons in a relevant age group. The values presented in the tables are the values of the dose absorbed in consequence of consumption of 1 kg of product, depending on a person's age.

Table 3

Comparison of effective weighted dose size obtained from the radionuclide ^{137}Cs after consumption of 1 kg of product by people of different age groups

Name of samples	Size of effective weighted dose $e(g)$ [nSv]					
Radionuclide	^{137}Cs					
Age	$g \le 1$ year	$g > 1$ year	$g = 2–7$ years	$g = 7–12$ years	$g = 12–17$ years	$g > 17$ years
Potato	12.2	7.0	5.6	5.8	7.54	7.5
Wheat	23.1	13.2	10.6	11.0	14.3	14.3
Barley	6.3	3.6	2.88	3.0	3.9	3.9
Sugar	3.8	2.1	1.7	1.8	2.3	2.3

Wheat contains the largest dose of radiation originating from ^{137}Cs. Potatoes and barley pearl provide considerably lower doses. The lowest doses are absorbed when consuming sugar. As the quantity of sugar in an average diet is much lower than other foodstuffs, the radiation dose supplied with it is relatively small.

Table 4

Comparison of effective weighted dose size obtained from the radionuclide ^{40}K after consumption of 1 kg of product by people of different age groups

Name of samples	Size of effective weighted dose *e*(*g*) [nSv]					
Radionuclide	^{40}K					
Age	$g \leq 1$ year	$g > 1$ year	$g = 2–7$ years	$g = 7–12$ years	$g = 12–17$ years	$g > 17$ years
Potato	39400	26600	13300	8240	4820	3930
Wheat	7300	4950	2470	1530	895	730
Rice	1410	958	479	296	173	141
Barley	6680	4520	2260	1400	819	668
Bean	30800	20900	10400	6450	3770	3080
Black bean	26500	18000	8990	5560	3250	2650
Oatmeal	7340	4970	2490	1540	900	734
Sugar	284	192	96.2	59.5	34.8	28.4

The seemingly largest radiation dose originating from ^{40}K is consumed with potatoes. As mentioned above, the activity measurements were made using dried potatoes. Usually, however, potatoes are not dried before consumption (except for potato crisps); one may assume 4 times lower value of the dose provided by fresh potatoes.

Considering the above, it can be assumed that the largest radiation dose is connected with consumption of white and red beans. Rice contains the least potassium; therefore, its consumption has the smallest influence on the absorbed dose size.

The analysis of data from Table 3 and 4 shows that an effective dose received after consumption of food containing both ^{137}Cs and potassium is much lower for caesium than the dose originating from the natural isotope ^{40}K. The dose, which source is potassium naturally present in food, is approximately 10^4–10^5 times bigger than the dose originating from artificial ^{137}Cs. When analysing the influence of an age group on a dose value, one can notice that in the case of isotope ^{137}Cs such a dose slightly decreases with age, however, in the case of natural isotope ^{40}K, the decrease is considerable.

It can be noticed that with the same level of nuclide activity penetrating the organisms of a child and adult, the child will receive a bigger dose. Due to the smaller total weight, the absorbed energy for one body weight unit will be higher for a child than for an adult.

On the basis of the data from Central Statistical Office in Poland [18], annual food consumption in Polish households in 2010 was estimated. Our estimates show that annual food consumption in 2010 is approximately 635 kg [1399.9354 pounds]/person. Figure 1 shows the correlation between the consumption volumes of the food contaminated with ^{137}Cs and the level of contamination, assuming that the limit dose of 1 mSv will be achieved (conversion index $1.3 \cdot 10^{-8}$).

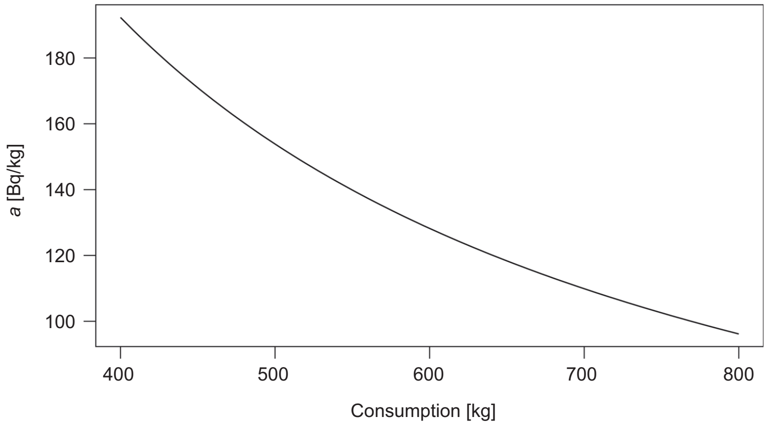

Fig. 1. Correlation between the consumption volume of the food contaminated with ^{137}Cs and the level of contamination, assuming that the limit dose of 1 mSv will be achieved (conversion index $1.3 \cdot 10^{-8}$)

The analysis of the graph in Figure 1 shows that consumption of *eg* 600 kg [1322.7736 pounds] of food during a year, with the activity of ^{137}Cs at approximately 130 Bq/kg, will result in absorbing the dose of 1 mSv, referred to in the Polish Regulation [7]. The largest activity of ^{137}Cs was noted in wheat. This activity is, however, two orders of magnitude lower than that, which could cause exceeding the allowed level of radiation dose, which originates from artificial sources. People absorb much larger radiation doses, which originate from natural sources rather than artificial ones. Apart from the natural isotopes present in food, people are exposed to radiation emitted by other unstable isotopes, in particular ^{222}Rn. Considering the above measurements of the analysed food products, one can note that they are not a major source of radiation for the population of the studied area. Despite the increased content of ^{137}Cs in many food products, radiation doses from that source are much lower than those allowed by the regulations. However, there are food products, which contain much higher than average activities of ^{137}Cs. This regards, for example, mushrooms – boletus species (*Xerocomus badius*), which activity could even exceed 1000 Bq/kg of dry mass [19]. Therefore, it is justified to implement tests for the presence of anthropogenic radiation isotopes in food products, which enable calculation of radiation doses received in consequence of food consumption.

Conclusions

Little activity of ^{137}Cs was confirmed in the analysed products. This illustrates the level of environment pollution with this isotope, and the possibility of its migration from soil to edible plants and food products.

The described studies showed that in consequence of consumption of food products, the inhabitants of the studied area may receive an increased radiation dose, which is one of the elements of the annual effective dose.

In the analysed foodstuffs, activities of natural isotope ^{40}K were much higher than ^{137}Cs. Taking into consideration other sources of ionising radiation, which are not present in food, one should assume that ^{137}Cs contained in food has a little share in the total radiation dose absorbed by people.

It could be stated that the detailed investigations of the ingested radiation dose rate related to the food consumption in the investigated area are not currently required. The simplified investigations can be temporarily repeated to detect possible changes in radioactive contamination in foodstuffs.

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BADANIE WCHŁONIĘTEJ SKUTECZNEJ DAWKI PROMIENIOWANIA OTRZYMANEJ WRAZ ZE SPOŻYWANĄ ŻYWNOŚCIĄ

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Abstrakt: Celem tego badania było określenie skutecznej dawki promieniowania jonizującego, pochłoniętej wskutek spożywania wybranych produktów żywnościowych. W ocenie ryzyka uwzględniono grupy wiekowe ludności. Badania przeprowadzono z wykorzystaniem produktów spożywczych, z których część została wyprodukowana na obszarach skażonych ^{137}Cs, uwolnionym po wybuchu elektrowni jądrowej w Czarnobylu. Wyniki przeprowadzonych badań potwierdzają zwiększenie dawki promieniowania, pochodzącej od sztucznych izotopów promieniotwórczych. Biorąc pod uwagę inne niż żywność źródła promieniowania jonizującego, można stwierdzić, że ^{137}Cs zawarty w artykułach spożywczych ma mały udział w całkowitej dawce promieniowania pochłoniętego przez mieszkańców badanego regionu.

Słowa kluczowe: ^{137}Cs, ^{40}K, żywność, dawka skuteczna promieniowania jonizującego

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THE OCCURRENCE OF PESTICIDES IN BERRY FRUITS FROM ORGANIC AND CONVENTIONAL CULTIVATION

WYSTĘPOWANIE ŚRODKÓW OCHRONY ROŚLIN W OWOCACH JAGODOWYCH Z UPRAW KONWENCJONALNYCH I EKOLOGICZNYCH

Abstract: Food from organic and conventional crops should retain sufficient nutritional value as well as a low content of substances which may pose a risk to health such as pesticide residues. The aim of the study was to determine and evaluate the residues of pesticides in raw berry fruits from organic and conventional crops from Podlasie region in Poland. The 141 samples of berry fruits from conventional crops and 61 samples of berry fruits from organic crops were collected in 2011: blackcurrant (57), redcurrant (26) and strawberry (119). The study included 160 pesticides, among which 28 were detected in the products of conventional crops, and 11 were found in the products from organic crops. During the study one detected the presence of substances whose use in plant protection is prohibited. Procymidone was found in 1 sample of blackcurrant. On the basis of conducted study a share of samples with multi-residues detected in the products was estimated: 21 % of the samples of organic crops contained from 2 to 5 residues, and 53 % of the samples of conventional crops contained from 2 to 9 residues. Because of the presence of residues of plant protection products in the organic products it is recommended to monitor food produced from these crops.

Keywords: pesticide residues, berry fruits, organic and conventional crops

The use of pesticides in conventional agriculture resulted in a significant increase in agricultural production and reduction of crop losses. However, the wide use of plant protection products has also disadvantages – there is the risk of residues in food and different elements of the natural environment, which can cause a variety of health effects. The risk arising from the use of pesticides affects mainly persons engaged in the distribution and production of these compounds, agricultural workers and those living in rural areas or eating contaminated food [1].

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In the recent years, organic farming has been promoted in Poland by governmental financial support which has been reflected in rural areas development plans. Polish farmers may apply for the European Union surcharges which are targeted at those who by the implementation of organic production not only produce high quality food, but also help to maintain biodiversity and protect natural resources [2]. According to Tomalak et al [3], organic production is considered to be the best system of farm management and food production that combines the best environmental practices, a high level of biodiversity, preservation of natural resources, application of high animal welfare standards and a production method corresponding to needs of certain consumers preferring products made from natural ingredients and as a result of natural processes. The main assumption of plant protection in organic farming is not to fight the diseases and pests, but creation the right conditions for plant growth, so that these factors could not develop in the crop or their impact on yield should be minimal. Organic products should not contain residues of other plant protection products, apart from those approved for use. The Maximum Residue Levels (MRLs) of plant protection products in organic farming are not standardized either in Poland or in the European Union, and even some countries believe that there is no need to normalize them [4]. Generally, residues should not be higher than the limit of detection [5].

The aim of this study was to evaluate and determine the residues of pesticides in raw berry fruits from organic and conventional crops from Podlasie region in Poland.

Materials and methods

The 141 samples of berry fruits from conventional crops and 61 samples of berry fruits from organic crops were collected in 2011: blackcurrant (57), redcurrant (26) and strawberry (119) from the Podlasie region in Poland. Pesticides (160 active substances) from various chemical and biological groups were investigated.

Berry fruits samples were obtained according the Polish norm [6] from the north-eastern Poland. The berry fruits samples were put into polyethylene bags and stored at –20 ^{o}C. Before the analysis they were thoroughly shredded and homogenized, except the analysis of dithiocarbamate residues where whole fruits were left.

The samples were analyzed by multi-residue method (MRM) by matrix solid phase dispersion method (MSPD), which is one of the most promising techniques to reduce matrix interferences. It involves dispersion of the sample over a solid support and subsequent elution with a relatively small volume of solvent [7, 8, 9].

The Pesticide Residues Laboratory (Białystok, Poland) is accredited according to PN-EN ISO/IEC 17025 by the Polish Centre for Accreditation and takes part in official food control every year [10]. The scope of accreditation covers different numbers of matrix/pesticide combinations. All the methods were validated. The quality of analytical methods is in compliance with the requirements of Document SANCO/10684/2009 [11].

An indispensable precondition for setting MRL is a risk assessment demonstrating consumer safety (consumer intake not exceeding the toxicological reference values).

The results under the limit of detection (LOD) of analytical methods used for intake calculations were taken as LOD values.

Results and discussion

Unlike most other chemical products, pesticides are deliberately released into the environment for controlling undesired organisms such as weeds, fungi and insects. Pesticides are biologically active compounds with a toxic component. They are regarded as significant sources of diffuse pollution that might cause long-term health implications in humans [12]. Among 141 samples from conventional farms, the remains of plant protection products were found in 78 samples. In 8 of them MRLs was exceeded, which constituted 5.7 %. In the 78 samples analyzed 28 active substances were detected. Table 1 presents the results of the analyzed samples according to assortment. Six pesticides exceeding MRL were observed: carbendazim and fenazaquin (in 2 samples), procymidone, cypermethrin, acetamiprid and propargite (each in 1 sample). During the study one detected the presence of substances whose use in plant protection is prohibited. It was procymidone, which was found in 1 sample of blackcurrant. According to Slowik-Borowiec et al [13], the presence of procymidone in the analyzed samples is associated with the widespread use of the preparations containing this substance in the recent years to effectively combat among others grey mould (*Botrytis cinerea*) in a wide range of fruit plants, vegetables and ornamentals. However, in the samples obtained from organic farms, plant protection products were found in 51 samples and 16 active substances were detected (Table 1, Fig. 1).

Table 1

Occurrence of pesticide residues in berry fruit from organic and conventional crops

Crop	Samples without residues	Fungicide		Insecticide	
		< MRLs	> MRLs	< MRLs	> MRLs
Organic crop					
Blackcurrant	2	2	0	0	0
Redcurrant	2	0	0	0	0
Strawberry	40	11	0	5	0
Conventional crop					
Blackcurrant	27	14	1	6	5
Redcurrant	2	13	1	11	1
Strawberry	54	20	0	6	0

According to Fernandes [14], although synthetic pesticides are not allowed for use in organic crops production, their sporadic presence of their residues can be readily explained. Organic and conventional agriculture usually takes place on adjoining farms, as a result of which the risk of cross-contamination cannot be excluded. Sometimes, the presence of pesticide residues in organic crops can also occur due to unlawful use of synthetic pesticides.

Pesticide residues were appraised according to the European Union Regulations [15] and compared with MRL. Maximum Residue Levels are the upper legal levels of concentration for pesticide residues in or on food or feed based on good agricultural practices, ensuring the lowest possible consumer exposure. Regulation (EC) No 396/2005 [16] establishes the MRLs of pesticides permitted in products of plant or animal origin intended for human or animal consumption. MRLs are derived after a comprehensive assessment of the properties of the active substance and residue levels resulting from the good agricultural practices defined for the treated crops. In Poland the year 2008 was very important for the harmonization of pesticide MRL legislation at the European level. Before September 1, 2008, a mixed system, with harmonized Community MRLs for about 250 active substances and national MRLs for the remaining substances, was applicable. When Regulation (EC) No 396/2005 [16] was introduced, it harmonized MRLs for all active substances used in plant protection products. According to Niewiadomska et al [17], one of the important measures to ensure food safety is constant control of pollutants. Such research is done not only to protect the health of consumers, but also to meet the quality requirements of food production both for the domestic market and the international.

Figure 1 illustrates all the detected active substances in the samples from organic crops. There were eight insecticides such as dimethoate, chloropyrifos, atrazine

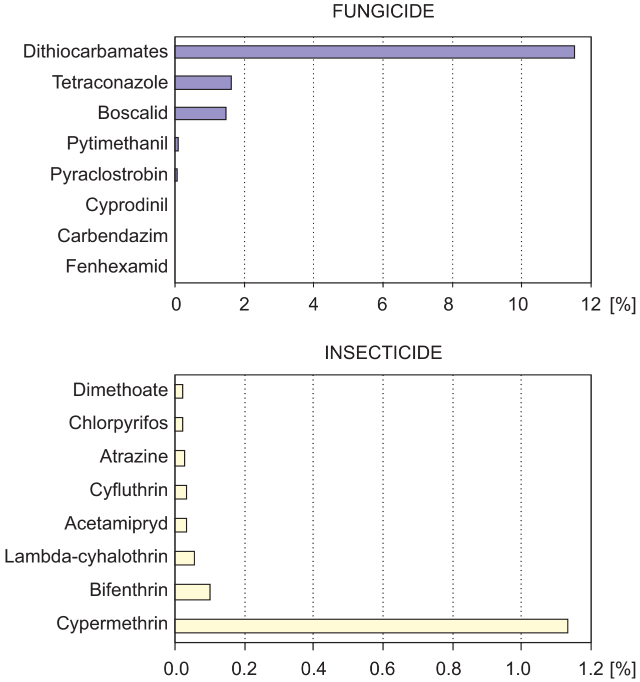

Fig. 1. Detected active substances of plant protection products in berry fruits from ecological crops

cyflutrin, acetamipryd, lambda-cyhalothrin, bifenthrin and cypermethrin, which were detected more than once. Moreover, eight fungicides such as dithiocarbamates, tetraconazole, boscalid, pyrimethanil, pyraclostrobin, cyprodinil, carbendazim and fenexamid were detected in the analysed samples. The highest concentration of fungicide, 3.05 mg · kg^{-1}, was observed for dithiocarbamates in a sample of strawberry. According to Claeys et al [17], dithiocarbamates have been widely used in the agricultural industry for 80 years. These compounds have shown wide applications as pesticides, fungicides in agriculture. Tetraconazole (fungicide) was detected at concentrations ranging from 0.01 to 1.07 mg · kg^{-1} (MRL = 0.2 mg · kg^{-1}), boscalid was found in 1 sample at concentration 1.9 mg · kg^{-1} (MRL = 0.05 to 10.00 mg · kg^{-1}). The highest concentration of insecticide 0.14 mg · kg^{-1} (MRL = 0.5 mg · kg^{-1}) was observed for bifenthrin in a sample of strawberry. Cypermethrin, the most commonly used insecticide in crops of berry fruits, was found in 5 samples at concentrations ranging from 0.002 to 0.02 mg · kg^{-1} (MRL = 0.02 mg · kg^{-1}) (Fig. 1).

Cypermethrin is important synthetic pyrethroid insecticide, extensively used in cotton, fruit and vegetable crops as well as in animal health, home and garden pest control worldwide [18]. As stated by Weston et al [19], the use of cypermethrin has increased sharply, especially over the recent years, with the restrictions or eliminations of highly toxic organophosphate pesticides, and it has become one of the dominant insecticides among retail sales to consumers.

In the tested samples from conventional farms captan, dithiocarbamates and boscalid were the most active substances detected among fundicide, while propagite and chlorpyrifos-ethyl among – insecticides. The highest concentration of fungicide, 3.42 mg · kg^{-1}, was observed for captan in a sample of blackcurrant. According to Barreda et al [20], captan is used to control fungal disease on a wide variety of crops. It acts through inhibition of a fungal process of respiration and metabolism through a non-specific thiol reactant. Although it is not a systemic fungicide, adjuvants can enhance transport of captan through a plant cuticle [21]. Teixeira et al [22] have found that levels of captan and procymidone residues were reduced by the pre-harvest intervals and/or culinary application, such as washing, peeling and storage. Boscalid is the second active substance which was detected at concentrations ranging from 0.02 to 0.99 mg · kg^{-1} (MRL = 0.05 to 10.00 mg · kg^{-1}). Dithiocarbamates was found in 18 sample at concentrations ranging from 0.05 to 1.49 mg · kg^{-1} (MRL = 5.00 mg · kg^{-1}) (Fig. 2).

Many authors [23–25] report that berry fruits have high levels of nutrients that are beneficial for health, a high water activity and low pH value, which makes blueberries particularly susceptible to fungal spoilage. To avoid it, the application of fungicides, as *eg* boscalid, is recommended for the prevention and treatment of grey mold (*Botrytis cinerea*) in fruit plants and vines.

Fungicides are considered to be non-selective and are used commonly to control a broad spectrum of plant diseases; hence, they have the potential to cause critical changes in soil microbial populations. It has been concluded by some authors that even a single application of fungicide at field rates may cause lasting changes in nitrogen transformations and availability in soils [26].

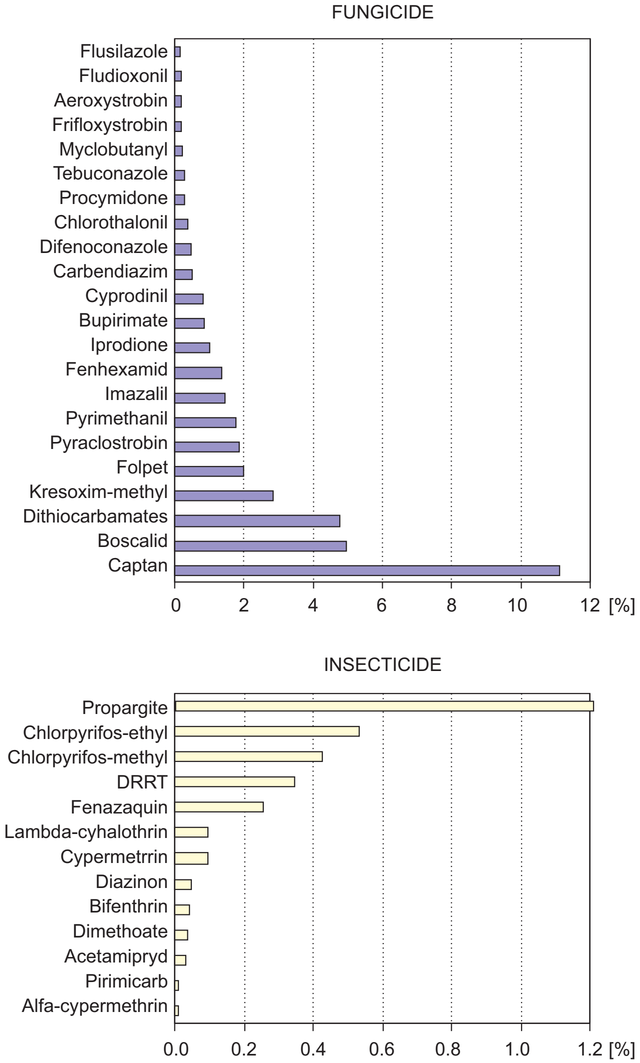

Fig. 2. Detected active substances of plant protection products in berry fruits from conventional crops

Another problem is multi-residue samples in plants. Although these effects are clearly observed in animal study for some substances, human epidemiological study have inherent limitations in identifying causes and effects of chronic exposures. A causal link between chronic exposure to pesticides and their possible health effects is difficult to establish because consequences appear years after a generally intense exposure or after repeated low-intensity exposures over many years [27].

During this period, 14.8 % (9 samples) of all samples were detected with one residue and 13.2 % (8 samples) contained more than one residue (from 2 to 5 active substances). Most samples contained two compounds, which constituted approximately

6.6 % (4 samples) of all samples, while four and five – 1.6 % (1 sample). Dithiocarbamates (F), tetraconazole (F) and cypermethrin (I) were the most often found combinations in the multi-residue samples from organic crops. Multi-residues were found most frequently in strawberry samples, which is in accordance with study conducted by Gnusowski et al [5]. The multi-residue samples are presented in Fig. 3.

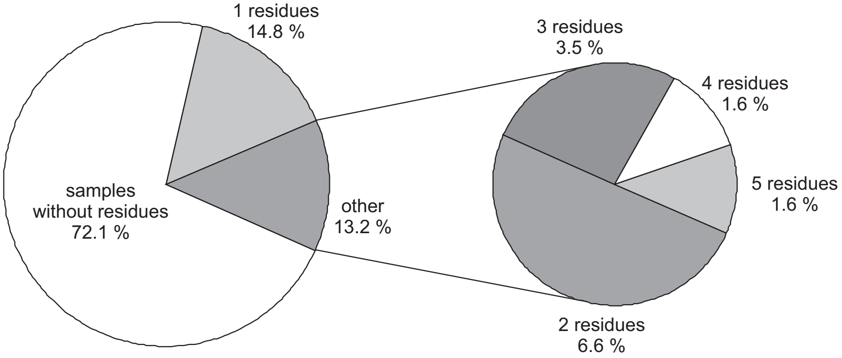

Fig. 3. Frequency of occurrence of samples without residues, with one residue, and with multi-residue in berry fruits from organic crops

According to Grosicka-Maciag [28], the occurrence of multiple residues in single crop samples can be the results many different factors, including the usage of pesticide formulations which contain more than one pesticide agent, the presence of certain persistent compounds in the environment, the application of various pesticides at different stages of growth and the mixture of different lots.

The results (Fig. 4) showed that the concentration of pesticide multi-residues in berry fruits amounted to 25.5 % (36 samples) of all samples were detected with one residue and 53.0 % (74 samples) contained more than one residue (from 2 to 9 active substances). Most samples contained two or three compounds, approximately 14.9 %

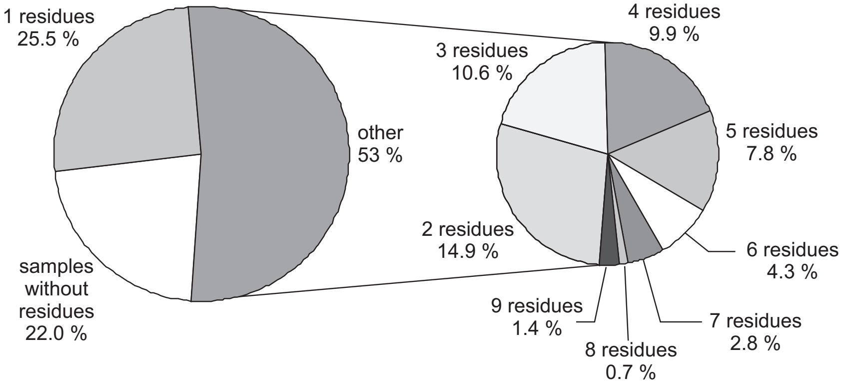

Fig. 4. Frequency of occurrence of samples without residues, with one residue, and with multi-residue in berry fruits from conventional crops

(21) and 10.6 % (15), while eight and nine – 0.7 % (1) and 1.4 % (2), respectively. Captan (F), boscalid (F), dithiocarbamates (F) and propargite (I) were the most often found in combinations in multi-residue samples from conventional crops.

Conventionally grown crops are expected to contain some pesticide residues because pesticides are used to control pests on these crops. The MRL values should be set at levels that are high enough to prevent chance of contravention if pesticides are used in compliance with good agricultural practice (GAP), but at the same time not so high that misuse will not be detected. In contrast, in the case of organically grown crops synthetic pesticides are not allowed, but as aforementioned, the presence of pesticides cannot be totally avoided due to circumstances that are beyond the control of the organic operator such as cross-contamination, especially from the earlier period, when pesticides were used on the fields. Nevertheless, samples of organic crops have apparently a much lower rate of pesticide residue findings compared with conventionally grown crops [29].

Conclusions

1. High percentage of berry fruits samples with residue below and above the allowed level (MRL) was observed in those samples taken from conventional crops.
2. High percentage of multi-residue samples was observed in the samples from organic crops. In terms of quality and food safety, multi-residues in berry fruits samples may carry increased risks to health of consumers, due to the overlapping various effects of the compounds characterized by different modes of action.
3. Due to the common occurrence of pesticide residue above MRL, prohibited pesticide and samples with multi-residues, berry fruits should be systematically monitored. Nevertheless, the results emphasize the need for continuous monitoring of pesticide residues in samples from organic crops for the purpose of authentication.
4. Due to the short growing season of berries and their instability, this study confirm the necessity of monitoring the correct performance of chemical treatments by farmers, in particular in conventional crops compliance with grace periods and manufacturers' instructions of plant protection products use.

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WYSTĘPOWANIE ŚRODKÓW OCHRONY ROŚLIN W OWOCACH JAGODOWYCH Z UPRAW KONWENCJONALNYCH I EKOLOGICZNYCH

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Abstrakt: Celem badań było określenie pozostałości pestycydów w świeżych owocach jagodowych z upraw ekologicznych i konwencjonalnych w województwie Podlaskim, Polska. Materiał do badań w 2011 r. stanowiło 141 próbek owoców jagodowych z upraw konwencjonalnych i 61 próbek z upraw ekologicznych, w tym: czarnej porzeczki (60), czerwonej porzeczki (25) i truskawek (119). Badaniami objęto 160 substancji aktywnych, z których 28 wykryto w produktach z upraw konwencjonalnych i 16 stwierdzono w produktach z upraw ekologicznych. Podczas badania wykryto obecność substancji, których stosowanie jako środków ochrony roślin jest zabronione. Do nich należy procymidon stwierdzony w 1 próbce porzeczki czarnej. Na podstawie przeprowadzonych badań oceniono udział próbek zawierających multipozostałości: od 2 do 5 pozostałości s.a. wykryto w 21,0 % produktów z upraw ekologicznych, a 53,0 % produktów z upraw konwencjonalnych zawierało od 2 do 9 pozostałości s.a. Ze względu na obecność pozostałości środków ochrony roślin w produktach ekologicznych zaleca się systematyczny monitoring żywności z tych upraw.

Słowa kluczowe: pozostałości pestycydów, owoce jagodowe, uprawy ekologiczne i konwencjonalne

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CONTENTS OF HEAVY METALS IN PLANTS AND SOIL FERTILIZATION OF ASH FROM SEWAGE SLUDGE COMBUSTION

ZAWARTOŚĆ METALI CIĘŻKICH W ROŚLINACH I GLEBIE NAWOŻONEJ POPIOŁEM ZE SPALANIA OSADÓW ŚCIEKOWYCH

Abstract: In the thesis assessed was fertilizing value of ashes from municipal sewage sludge combustion in grate furnace in Pomorzany Sewage Treatment Plant in Szczecin. The ash was treated as a substitute of phosphorus from phosphatic fertilizer because general content of this component exceeded 20 % of P_2O_5. In 2011–2012 a field experiment was conducted on a light soil. The scheme of the experiment included five objects of fertilizing corn for seeds and spring rape with mineral fertilizers (NK, NPK) and mineral fertilizers together with increasing doses of ash from municipal sewage sludge combustion (NK + P1, NK + P2, NK + P3). Substitution of phosphorus in a dose of NPK from superphosphate enriched with phosphorus from ash (P1, P2, P3) from municipal sewage sludge combustion did not cause any differences in the volume of corn seeds or corn stove or rapeseed straw, and in the object NK + P3 received were considerately richer crops with spring rape seeds than from any other objects. Ahs caused an increase in content of cadmium and nickel in seeds and straw, as for lead only in corn seeds, content of cadmium and lead in spring rape seeds and cadmium in straw. After two years of applying nitrogen and potassium as mineral fertilizers and ashes from municipal sewage sludge combustion, in comparison with exclusive fertilizing corn and spring rape with mineral fertilizers, an increase of lead in general soil content was observed, and general content of cadmium and nickel as well as their dissoluble form in 1 molHCl $\cdot$ dm^{-3} in soil from all objects was similar.

Keywords: municipal sewage sludge, ash from sludge, Cd, Ni, Pb, plants, soil

Introduction

The intention to implement a prohibition to store municipal sewage sludge at municipal landfill site forces to search for a new solutions to manage it, taking into

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consideration the following aspects: ecological, technical and economic. Bien et al [1] state that sludge, after having been processed, should come back to the environment, mostly because its agricultural use is recommended to small and medium treatment plants, and for big treatment plants other solutions should be searched for. Agricultural use of municipal sewage sludge can still have a major meaning when it comes to light soils [2] and with fertilizing energy plants [3].

According to Pajak [4] strategy of sewage sludge management with thermal ways, acknowledged by big and medium national aglomerations, is fully legitimate. According to the author, Switzerland is an example confirming this direction because 97 % of sludge there is processed thermally, and it is not used agriculturally at all. In Germany *ca* 20 % is managed agriculturally, yet simultaneously *ca* 50 % is processed thermally, at the same time in Poland only 1 % of sewage mass was a subject to such a process.

Thermal processing of sewage sludge by combustion is not neutral for the environment because during combustion gasses are produced which get contaminated with speck, carbon monoxide, nitrogen oxide, sulphur oxide as well as atypical mineral acids, heavy metals and hydrocarbons [5]. Sewage sludge combustion generates a new kind of waste – ash – which needs to be managed. From Kosior-Kazubek and Karwowska's [6] researches it results that ash from sewage sludge combustion can be used as an active component substituting a part of cement in mortars.

Dependent on chemical composition of sludge, as well as technical solutions in its thermal utilisation, ash with different content of macro- and microelements, including heavy metals, is received. The thesis touches upon an attempt to assess fertilizing value of ash from sewage sludge combustion in municipal grate furnace in "Pomorzany" Treatment Plant in Szczecin. Ash was treated as a substitute of phosphorus from phosphatic fertilizer because the general content of this component exceeded 20 % of P_2O_5. Moreover, phosphorus among basic macroelements (N, P and K) is the most expensive one and its alternative sources should be searched for.

Material and methods

In the time period of 2011–2012 in Agricultural Experimental Station in Lipnik, which is located near Stargard Szczeciński, tests with the use of ash from municipal sewage sludge combustion for fertilizing plants were conducted. Field experiment was performed on rusty soil, incomplete, received from clayey sand which is light and dusty, planted on average depth with light clay (valuation class IVb, good rye complex – 5, soil category – light soil). Before the experiment started soil pH was slightly acidic (5.8 pH in 1 molKCl $\cdot$ dm^{-3}), total content of carbon amounted to 8.59 g $\cdot$ kg^{-1}, nitrogen 0.84 g $\cdot$ kg^{-1}, easily assimilated form was high for phosphorus, and low for potassium and magnesium.

Total content of trace elements in soil amounted to: 254.7 mgMn, 62.31 mgZn, 6.439 mgCu, 8.320 mgNi, 0.554 mgCd and 5.215 mgPb $\cdot$ kg^{-1} d.m.

Scheme of tests included five forms (in 4 repetitions) of fertilizing with mineral fertilizers and ash from municipal sewage sludge combustion: NK, NPK, NK + P1 (P1 – 1 ash dose), NK + P2 (P2 – 2 ash dose), NK + P3 (P3 – 3 ash dose) corn for seeds and spring rape. Pre-sowing mineral fertilizing with nitrogen under both plants was used as ammonium sulphate (20 % of N), and topdressing fertilizing with ammonium sulphate (34 % of N). Phosphorus (enriched superphosphate 40 % of P_2O_5) and potassium (potassium salt 60 % of K_2O) and in mineral fertilizers were used yearly only for pre-sowing fertilizing. Ash from municipal sewage sludge combustion, which constitutes a substitute for phosphatic fertilizer, comes from "Pomorzany" Sewage Treatment Plant in Szczecin. In both years of research, the same ash was applied for pre-sowing fertilizing and its chemical composition was shown in Table 1.

Table 1

Chemical composition of ash from municipal sewage sludge combustion

Content of forms soluble			Total content of								
in strong mineral acids	in 2 % citric acid	in water	K	Ca	Mg	Cd	Cu	Mn	Ni	Pb	Zn
[% P_2O_5]			[$g \cdot kg^{-1}$]			[$mg \cdot kg^{-1}$]					
22.05	12.08	7.64	42.6	62.2	38.7	4.16	476.2	411.4	74.7	93.0	745.1

Experiment plants in both years were corn and spring rape, which in the first year was cultivated on soil on which winter wheat had been cultivated before, and in the second year spring rape was cultivated after corn, and then after spring rape was corn and after corn spring rape again. Corn for seeds (varieties DKC 3016 – FAO 240) was sown in the first year on 28.04., and in the second on 05.05. in the number of 75 thousand seeds per ha. Under corn pre-sowing fertilizers were used as following: 40 kg N, 50 kgP_2O_5, 110 kg$K_2O \cdot ha^{-1}$, and with further doses of ash applied was 50, 100 and 150 kg of $P_2O_5 \cdot ha^{-1}$. For topdressing fertilizing (in 6–7 leaf stage) 40 kg$N \cdot ha^{-1}$ was used. During vegetation, corn was two times protected against pests and one time weeds were destroyed. Harvesting of all corn plants was done manually (18.10.2011 and 04.10.2012), and then corn cobs were separated from other parts of the plants. After cobs being treshed manually, mass of corn seeds and straws was determined, to straws stems, rachis and seed covers from cobs.

Spring rape ('Lariss' variety in 2011 and 'Markus' variety in 2012) was sown in the first year on 20.04., and in the second year on 10.04. For spring rape the following pre-sowing fertilizing was used: 50 kgN, 50 kgP_2O_5, 120 kg$K_2O \cdot ha^{-1}$, and in further doses of ash applied was 50, 100 and 150 kg of $P_2O_5 \cdot ha^{-1}$. For topdressing fertilizing (in the green bud stage) applied was 50 kg of $N \cdot ha^{-1}$. Moreover, during vegetation spring rape was sprayed against rape beetle and weeds were also destroyed. Spring rape harvesting was done by a combine harvester on 26.08.2011 and 19.08.2012.

After harvesting, the mass of crop was determined, samples were taken and initially dried in the temperature of 60 ^oC. Content of dry mass was marked using oven-drying method and total content of Cd, Ni, and Pb was marked with an ASA method in the dried samples, after prior mineralization of the samples in mixture (3:1, *v*/*v*) of nitric acid and chloric(VII) acid. After harvesting of spring rape and corn in 2012, samples of soil were taken from four repetitions of each fertilizing object, the samples were mixed and average object samples were received. Prior to marking the total content of heavy metals in soil, it was mineralized in the same acids but mixed in 1:1 relation. Variation analysis of corn and spring rape crop results was done in randomized block system according to FR-ANALWAR package. Multiple comparisons of the average were done by using Tukey's procedure with significance level of $\alpha \le 0.05$. Standard deviation for content of heavy metals in plants and soil was determined according to STATISTICA 10 program.

Results and discussion

In Poland, for over a dozen years, a dynamic increase in agricultural areas cultivation of corn for seeds has been observed, which can be associated a /o with the possibility of using seeds for bioethanol production. In 2012, participation of this plant in grain sown structure constituted 7 % (539 thousand ha), and an average seed crop constituted *ca* 6 $\mathrm{Mg \cdot ha^{-1}}$ [7].

In the discussed researches in both years a richer crop of corn seeds was received – 75 and 95 %, respectively (Table 2) when compared to the national average.

Tabela 2

Seeds and straw crop of corn and spring rape [$\mathrm{Mg \cdot ha^{-1}}$]

Objects	Maize						Spring rape					
	corn			straw			seeds			straw		
	2011	2012	$\bar{x}$	2011	2012	$\bar{x}$	2011	2012	$\bar{x}$	2011	2012	$\bar{x}$
NK	10.13	11.99	11.06	10.06	11.21	10.64	0.51	1.67	1.09	6.25	5.84	6.05
NPK	10.33	11.08	10.71	9.21	11.73	10.47	0.50	1.76	1.13	6.42	5.84	6.13
NK-P1	11.01	12.23	11.62	9.65	12.14	10.90	0.51	1.75	1.13	6.59	5.67	6.13
NK-P2	10.29	11.21	10.75	9.45	11.77	10.61	0.55	1.80	1.17	6.17	5.67	5.92
NK-P3	10.68	11.93	11.31	9.90	12.26	11.08	0.64	1.84	1.24	6.67	5.92	6.30
Average	10.49	11.69	11.09	9.17	11.82	10.50	0.54	1.76	1.15	6.42	5.79	6.11
$\mathrm{LSD_{0.05}}$	n.s.*	n.s.	n.s.	n.s	n.s	n.s	0.075	0.077	0.049	n.s.	n.s.	n.s.

* n.s. – non significant.

In respecive years, as an average crop from the two years of research was not particularly diversified between objects fertilized with mineral fertilizers (NK and NPK) and objects fertilized with mineral fertilizers with the addition of ash from municipal sewage sludge combustion (NK-P1, NK-P2 and NK-P3). The richest average crop of seeds was harvested from the object where nitrogen and potassium were used as mineral fertilizers and phosphorus in the form of ash (P1) in a dose of 50 kg of $\mathrm{P_2O_5 \cdot ha^{-1}}$ (11.62 $\mathrm{Mg \cdot ha^{-1}}$), on other objects crops of seeds was poorer ranging from 0.31 to 0.87 $\mathrm{Mg \cdot ha^{-1}}$. Applied fertilizing with mineral fertilizers and ash from municipal sewage sludge combustion did not differeniate crops of corn straw meaningfully (Table 1), and the richest average crop of corn was harvested from object NK-P3 (11.08 Mg · ha^{-1}), the poorest from object NPK (10.47 Mg · ha^{-1}). Average crop of corn harvested in the research by Burczyk [8] resulted 9.96 Mg · ha^{-1} in seeds, and 22.10 Mg · ha^{-1} in straw. In a research by Meller and Bilende [9], where ash from biomass combustion was used for fertilizing corn, average crop of fresh corn mass totalled 75.0 Mg · ha^{-1}. The best effects of plants' growth were achieved with the dose of 60 Mg · ha^{-1} of ash.

In the last years also agricultural area for cultivation of spring rape and agrimony has increased and in 2012 constituted 6.9 %. Still, spring rape represents minor percentage in agricultural area of oil plants, due to its poorer cropping than winter rape.

In 2011, in the following research received was on average *ca* 3 times poorer crop of spring rape seeds (0.54 Mg · ha^{-1}) than in 2012 (1.76 Mg · ha^{-1}), which was a result of long-lasting drought in the flowering period and seeds forming time of spring rape. The richest crop of seeds in this year was harvested from object NK-P3 (0.64 Mg · ha^{-1}), which was highly different from crops from other objects. In the second year of research, a similar dependence was observed, because from the above mentioned object, the richest crop of seeds was harvested (1.84 Mg · ha^{-1}), but it was not significantly richer than crops from objects NK-P1, NPK and NK. Average crop of seeds from the two years of research from object NK-P3 was the richest and indeed exceeded crops from other objects by 8.7 %. Applied fertilizers did not differentiate crops of spring rape straw significantly, taking into consideration that the richest average crop, similarly to seeds, was recived from object NK-P3 (6.30 Mg · ha^{-1}).

Fertilizing with mineral fertilizers and ash from municipal sewage sludge combustion, in comparison to exclusive fertilizing with mineral fertilizers, differentiated content of analysed heavy metals in most cases (cadmium, nickel and lead) in seeds and straw of corn and spring rape. Content of heavy metals in biomass of both plants was presented as weighted average from the two years of research (Table 3).

Tabela 3

Weighted average (from the two years) content of trace elements in seeds and straw of corn and spring rape

Objects	Maize						Spring rape					
	corn			straw			seeds			straw		
	[mg · kg^{-1} d.m.]											
	Cd	Ni	Pb	Cd	Ni	Pb	Cd	Ni	Pb	Cd	Ni	Pb
NK	0.325	0.380	2.45	0.571	0.278	2.76	0.562	2.63	1.77	0.713	1.42	2.68
NPK	0.306	0.372	2.49	0.616	0.324	2.76	0.574	2.86	1.66	0.701	1.48	2.51
NK-P1	0.472	0.341	3.13	0.724	0.315	2.35	0.730	2.86	1.70	0.821	1.35	2.56
NK-P2	0.405	0.547	3.01	0.559	0.528	2.38	0.678	2.83	1.84	0.871	1.56	2.52
NK-P3	0.460	0.646	3.16	0.652	0.424	2.46	0.697	2.64	1.89	0.892	1.54	2.55
Average	0.393	0.456	2.85	0.624	0.374	2.53	0.650	2.76	1.77	0.800	1.47	2.56
Standard deviation	0.077	0.133	0.350	0.067	0.102	0.203	0.076	0.118	0.095	0.088	0.087	0.068

Content of cadmium in corn seeds from all objects fertilized with mineral fertilizers (NK) and ash from municipal sewage sludge combustion was significantly higher (on average by 45.8 %) than in seeds from objects NPK. An increase in content of nickel in seeds from objects NK + ash, when compared to NPK, was observed after application of two bigger doses of ash (P2 – 100 and P3 – 150 kg of $P_2O_5 \cdot ha^{-1}$) by 47.0 and 73.7 %, respectively. All doses of ash with NK, in relation to NPK increased (on average by 24.5 %) the content of lead in corn seeds. The highest content of cadmium was observed in corn straw harvested from object NK-P1 (0.724 $mgCd \cdot kg^{-1}$ d.m.). In straw from other objects, content of cadmium was lower (by 9.9 to 22.8 %). For more significant increase in content of nickel in corn straw, similarly to seeds, in comparison to NPK, two bigger doses of ash had influence, which caused an increase in content of this metal by 63.0 and 30.9 %. Fertilizing with ash from municipal sewage sludge combustion did not differentiate significantly the content of lead in corn straw. Average content of lead in objects with ash totalled 2.40 $mgPb \cdot kg^{-1}$ d.m., and in straw from object NPK was higher by 13.0 % when compared to objects fertilized with ash. In the research by Meller and Bilende [9] average content for nickel from objects fertilized with ash from biomass combustion in corn seeds amounted to 3.78, for cadmium 0.37 $mg \cdot kg^{-1}$, and for straw 9.12 and 0.44 $mg \cdot kg^{-1}$, respectively.

In seeds of spring rape from objects fertilized with nitrogen and potassium as mineral fertilizers, and phosphorus as ash from municipal sewage sludge combustion an increase in content of cadmium, in relation with NPK, was observed on average by 22.3 %, taking into consideration that the highest advance (by 27.2 %) was caused by the slightest dose of ash (Table 3). Content of nickel in spring rape seeds was slightly differentiated by mineral fertilizers and ash, and average content oscilated from 2.63 to 2.86 $mgNi \cdot kg^{-1}$ d.m. On the other hand, content of lead, as a result of fertilizing NK and ash in comparison to NPK, increased on average by 9.0 %. In spring rape straw, content of cadmium increased along with the increase of ash dose, and average advance in comparison to NPK amouted to 22.8 % (Table 3). Increase in content of nickel in srping rape straw on the objects NK + ash in relation to objects NPK was observed after second and third dose of ash was applied, but it was sligt (on average *ca* 5.0 %). Content of lead in spring rape straw was slightly differentiated and oscilated from 2.51 to 2.68 $mgPb \cdot kg^{-1}$ d.m.

Table 4 presents an average total content of heavy metals and their forms dissolved in 1 $molHCl \cdot dm^{-3}$ in soil sampled from 0–20 cm layer from objects fertilized with mnineral fertilizers and ash in the second year of corn and spring rape cultivation.

In relation to object fertilized with mineral fertilizers (NK and NPK) in soil from objects NK + ash, an average increase in total content of cadmium reached barely 2.81 %. A slight increase in cadmium and nickel content in soil is a result of application of those small amounts of heavy metals to soil with ashes. And average content of cadmium forms dissolved in 1 $molHCl \cdot dm^{-3}$ in objects NK + ash was higher only when compared to content determined in soil fertilized with NK. Average total content of nickel in soil from individual fertilized objects was barely differentiated (from 7.33 to 7.65 $mgNi \cdot kg^{-1}$ d.m.), similarly to forms of nickel dissolved in 1 $molHCl \cdot dm^{-3}$

(from 0.611 to 0.681 mgNi · kg^{-1} d.m.). A slight increase of cadmium and nickel in soil is a result of application of small amounts of those heavy metals to the soil with ashes.

Tabela 4

Total content of heavy metals and their forms dissolved in 1 molHCl · dm^{-3} in soil from 0–20 cm layer [mg · kg^{-1} d.m.] after two years of fertilizing with ash from municipal sewage sludge combustion

Objects	Cd		Ni		Pb	
	total content	soluble forms	total content	soluble forms	total content	soluble forms
NK	0.563	0.144	7.58	0.681	5.15	2.79
NPK	0.575	0.170	7.65	0.656	5.67	3.19
NK-P1	0.568	0.159	7.33	0.631	6.24	2.74
NK-P2	0.585	0.173	7.53	0.611	6.28	2.78
NK-P3	0.568	0.171	7.45	0.621	6.59	2.85
Average	0.572	0.164	7.51	0.640	5.99	2.87
Standard deviation	0.008	0.012	0.123	0.028	0.573	0.183

A major increase in total content of lead in fertilized soil with NK and ash was observed, which in relation to object NK reached on average 23.7 %, and in relation to NPK 12.3 %. Content of lead forms dissolved in 1 molHCl · dm^{-3} in soil from objects NK + ash was approximate to content from object NK, and lower than in soil fertilized with NPK. The highest average paticipation of heavy metals forms dissolved in 1 mol HCl · dm^{-3} in its total content in soil was observed in case of lead (47.9 %), lower for cadmium (28.7 %), and the lowest for nickel (8.52 %).

According to Regulation of Minister of Environment in case of waste catalogue [10] grated slags and ashes from municipal sewage sludge combustion can be classified as combustion slags and ashes, code 19 01 12 (other than mentioned in 19 01 11). Those, however, cannot be recycled R10 according to Regulation of Minister of Environment in case of the process of recycling R10 [11].

Usefullness of ashes from minicipal sewage sludge combustion for agricultural use in literature is estimated on the basis of their psychic-thermal properties and chemical composition. Information provides that ashes are poor in nitrogen and rich in phosphorus, calcium and magnesium, but at the same time they can have higher content of heavy metals [6, 12]. Ash used in own research did not contain particularly high contents of studied heavy metals (Cd, Cu, Ni, Pb and Zn) and did not exceed admissible contents determined in Regulation of Minister of Environment on municipal sewage sludge [13]. Phosphorus, which can be found in ash, can have an important fertilizing meaning, but which has been barely used as fertilizer in recent years. Ottosen et al [14] research gives evidence that ash from municipal sewage sludge combustion may be a significant source of phosphorus, and Wzorek et al [15] maintain the same about ashes from co-combustion of waste from meat processing industry and municipal sewage sludge. The last mentioned authors, at 1:1 relation of both components, received ash of over 10 % of P content.

Conclusions

1. Substitution in the dose of NPK of phosphorus from superphosphate enriched with phosphorus from municipal sewage sludge combustion ash did not cause any significant differences in the crop volume of corn and spring rape seeds and straw. However, average crop of spring rape seeds from object NK with the highest dose of phosphorus from ash significantly exceeded crops from other objects.
2. Mineral fertilizing with nitrogen and potassium as mineral fertilizers and ash from municipal sewage sludge combustion caused an increase in content of cadmium and nickel in seeds and straw, lead content only in corn seeds, content of cadmium and lead in spring rape seeds, and cadmium in straw.
3. After two years of applying nitrogen and potassium as mineral fertilizers and ash from municipal sewage sludge combustion, in comparison to exclusive fertilizing of corn and spring rape with mineral fertilizers, an increase in total content of heavy metals in soil was observed, and total content of cadmium and nickel, as well as their forms dissolved in 1 molHCl · dm^{-3} was on similar level in soil from all objects.

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ZAWARTOŚĆ METALI CIĘŻKICH W ROŚLINACH I GLEBIE NAWOŻONEJ POPIOŁEM ZE SPALANIA OSADÓW ŚCIEKOWYCH

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Abstrakt: W pracy podjęto próbę oceny wartości nawozowej popiołu pochodzącego ze spalania w piecu rusztowym komunalnych osadów ściekowych w Oczyszczalni „Pomorzany” w Szczecinie. Popiół potraktowano jako substytut fosforu z nawozów fosforowych, gdyż ogólna zawartość tego składnika przekraczała 20 % P_2O_5. W latach 2011–2012 przeprowadzono doświadczenie polowe na glebie lekkiej. Schemat badań obejmował pięć wariantów nawożenia kukurydzy na ziarno i rzepaku jarego nawozami mineralnymi (NK, NPK) oraz nawozami mineralnymi ze wzrastającymi dodatkami popiołu ze spalania komunalnych osadów ściekowych (NK + P1, NK + P2, NK + P3). Zastąpienie w dawce NPK fosforu z superfosfatu wzbogaconego fosforem z popiołu (P1, P2, P3) ze spalania komunalnych osadów ściekowych nie spowodowało istotnych różnic w wielkości plonu ziarna i słomy kukurydzy oraz słomy rzepaku jarego, a na obiekcie NK + P3, uzyskano istotnie większy plon nasion rzepaku niż z pozostałych obiektów. Stosowanie popiołu skutkowało zwiększoną zawartością kadmu i niklu w ziarnie i słomie, a ołowiu tylko w ziarnie kukurydzy oraz zawartości kadmu i ołowiu w nasionach rzepaku jarego i kadmu w słomie. Po dwóch latach stosowania azotu i potasu w postaci nawozów mineralnych i popiołu ze spalania komunalnych osadów ściekowych, w porównaniu z wyłącznym nawożeniem kukurydzy i rzepaku jarego nawozami mineralnymi, odnotowano zwiększenie całkowitej zawartości ołowiu w glebie, natomiast całkowita zawartość kadmu i niklu oraz ich form rozpuszczalnych w 1 mol HCl $\cdot$ dm^{-3} w glebie wszystkich obiektów była podobna.

Słowa kluczowe: komunalne osady ściekowe, popiół z osadów, Cd, Ni, Pb, rośliny, gleba

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CONTENT RATING OF CHOSEN TRACE ELEMENTS IN PLANTS AND SOIL AFTER APPLICATION OF NEWSPAPER WASTE

OCENA ZAWARTOŚCI WYBRANYCH PIERWIASTKÓW ŚLADOWYCH W ROŚLINACH I GLEBIE PO APLIKACJI PAPIERU GAZETOWEGO

Abstract: The research was conducted to determine the content of Cr, Cd, Ni and Pb in soil and plant biomass after application of newspaper waste. The pot experiment was conducted in the years 2010 and 2011 in the greenhouse and included the following objects: NP-0 soil without addition of newspaper, NP-1 the soil with addition of 1 % of newspaper and NP-3 the soil with addition of 3 % of newspaper. Addition of newspaper was calculated relative to the dry weight of the soil material. The study was conducted in pots containing 5.50 kg of air-dried soil material. Two plants were grown in the experiment: spring rape, ‘Felix’ c.v., in the first year and naked oats, ‘Siwek’ c.v., in the second. Rape was collected at the end of the flowering stage (73-day vegetation period), and oats at grain milk stage (75 days of vegetation). After preparation of plant material and soil, content of trace elements was determined by ICP-OES method on a Perkin Elmer Optima 7300DV apparatus. The results were converted to absolute dry weight of the material.

Application of newspaper to soil did not increase (except for cadmium) the contents of lead, chromium or nickel in the aboveground parts of the plant. Studied trace elements were accumulated mainly in the plant roots. Roots contained on average from 51 to 82 % more of the test elements in relation to the aboveground parts. Higher amount of newspaper (3 %) added to the soil led to a higher accumulation of studied trace elements in the roots and lower in the plant aboveground parts. The addition of newspaper to the soil caused a reduction in acidity. Newspaper introduced to the soil generally did not increase the total content of trace elements.

Keywords: newspaper, soil, plants, trace elements

Introduction

Paper belongs to the biodegradable wastes which in compliance with act on wastes should not be deposited in landfills [1]. It has been estimated that in the EU countries

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about 60 % of the total annual production of paper finds its way to landfills, of which on average 4 % is a newsprint [2]. Seeking the opportunities for repeated use of material of low suitability for recycling makes necessary finding new solutions allowing to reduce the biodegradable biomass which is deposited in landfills. Newsprint manufactured from recycled paper may provide a potential raw material enriching soil in organic matter. An additional asset of the paper is wide C:N ratio (398-852:1) [1]. Another opportunity of newspaper management may be its composting with other biodegradable wastes [4]. A supplement of such component to the composted biomass may improve the conditions for the process (mainly due to decrease in water content) and in result improve the structure of produced wastes. However, it should be remembered that an addition of newspaper fraction to the soil or composted fraction of biodegradable waste may also generate negative results. An example of unfavourable effect of newspaper on the soil environment or generated biomass may be an increase in trace element contents, which constitute an integral part of newspaper inks [5].

The investigations aimed at an assessment of Cr, Cd, Ni and Pb contents in the soil and plant biomass after the application of newspaper.

Material and methods

The research on the effect of newspaper application on the content of selected trace elements in the soil and plant biomass was conducted in 2010–2011 as a pot experiment in the vegetation hall of the Faculty of Agriculture and Economics, University of Agriculture in Krakow.

The experimental design comprised three objects in 4 repetitions: NP-0 – control (soil without newspaper supplement), NP-1 – soil with 1 % admixture of newspaper and NP-3 – soil with 3 % addition of newspaper. Newspaper supplement was calculated in relation to the soil material dry weight. Newspaper mass before the application to the soil was crushed mechanically in paper shredder. Characteristics of selected properties of the newspaper used for the experiment were shown in Table 1.

Table 1

Selected properties of newspaper and soil before experiment (0–20 cm)

Determination	Unit	Newspaper	Soil
pH in H_2O	—	6.25 ± 0.03	n.d.
pH in KCl	—	n.d.	5.81 ± 0.22
Electrolytic conductivity	$[mS \cdot cm^{-1}]$	7.41 ± 0.04	0.12 ± 0.01
Organic C	$[g \cdot kg^{-1}$ d.m.]	294 ± 4	9.08 ± 0.48
Total N		16.4 ± 0.1	1.16 ± 0.03
Total Ni	$[mg \cdot kg^{-1}$ d.m.]	22.0 ± 0.2	9.88 ± 0.25
Total Cr		45.0 ± 3.3	13.2 ± 0.5
Total Cd		0.10 ± 0.07	1.00 ± 0.07
Total Pb		1.36 ± 0.27	25.4 ± 1.1

± standard deviation, n = 2; n.d. – not determined.

The experiment was conducted in plastic pots containing 5.50 kg of air-dried soil material. The soil material was ordinary loam collected from 0–20 cm arable layer of ploughland located at the experimental station of the University of Agriculture in Mydlniki. Selected properties of the soil material prior to the investigations were assessed using methods commonly applied in agricultural chemistry [6]. Properties of the soil materials were presented in Table 1.

In the first year of research the test crop was spring rape, 'Feliks' c.v., and in the second naked oats, 'Siwek' c.v. Rape was harvested by the end of flowering stage (73 days of vegetation), while rape at grain milk maturity (75 days of vegetation). The plants were harvested and divided into aboveground parts and roots. The plant material was dried at 70 ^{o}C in a drier with air flow and the dry weight yield was determined. Then it was ground in a laboratory mill and subjected to chemical analyses. Biomass obtained from the test plants was subjected to independent chemical analyses when the subsequent vegetation seasons of rape and oats ended. Mean weighted contents of analysed trace elements were computed from the results obtained for both plants.

Dried and ground plant material was mineralized in a chamber furnace (at 450 ^{o}C for 5 h). The remains were dissolved in diluted nitric acid (1:2, *v*/*v*) [6]. The content of nickel, chromium, cadmium and lead in the obtained solutions was assessed by means of ICP-OES method on Perkin Elmer Optima 7300DV apparatus and the obtained results were conversed into the plant material absolute dry mass.

The soil material was collected after each year of the experiment, dried at room temperature, crushed in a porcelain mortar and sifted through a sieve with 1 mm mesh. In the material prepared in this way pH was determined by potentiometer in the suspension of soil material and 1 mol $\cdot$ dm^{-3} KCl solution, electrolytic conductivity by conductometer and the content of total trace elements after organic substance incineration in a chamber furnace (at 500 ^{o}C for 8 hours) and mineralization of the residue in a mixture of concentrated nitric and perchloric acids (2:1, *v*/*v*). The concentrations of analysed elements were assessed in the obtained solutions using ICP-OES method on Perkin Elmer Optima 7300DV apparatus.

A one-way ANOVA in the completely randomized design using f-Fisher test was conducted for the obtained results. The significance of differences between arithmetic means was verified on the basis of homogenous groups created by Tukey's test at the significance level $\alpha \leq 0.05$. All statistical computations were made using Statistica PL packet [7].

Results and discussion

Biodegradation of newspaper waste in soil is a complicated process, primarily basing on lignin degradation. The content of this component may reach even 20 % of dry matter [8]. Research of Tuomela et al [4] show that the theoretical degree of paper biodegradation at 15 % content of lignin is 41 %. Considering the fact that humus is formed mainly of lignin, the share of the other paper components, such as cellulose or hemicellulose is less important [9].

Paper is a material which, due to a considerable proportion of complex organic compounds (lignin), does not undergo a total mineralization. It decomposition is conducted primarily by thermophilous fungi and actinomycetes [4]. It is believed that the microorganisms capable of cellulose hydrolysis, responsible for paper biodegradation appear already at the stage of production. Their destructive effect on newspaper is much more serious than in case of other paper wastes. It is caused not only by the paper weight itself, but also the kind of raw material of which it was manufactured. In case of newspaper, which is a recycled product (recycled paper), low quality of the raw product which weakens the final product, is visible [10]. Development of cellulolytic fungi causes not only changes on the paper surface but also leads to chemical and physical changes in its structure [11]. The outcome of the changes may be accelerated migration of trace elements present in printers ink to the soil solution.

Trace elements penetrating into the soil with applied material may undergo various changes. These changes may have a significant influence on the quantity of compounds directly available to plants [12, 13].

Presented research has shown that the highest total amount of plant biomass was obtained in the object where no newspaper was supplied (NP-0). Significantly the smallest biomass amount was harvested from the object where 3 % of newspaper supplement was added (NP-3) in relation to the soil material dry weight (Fig. 1).

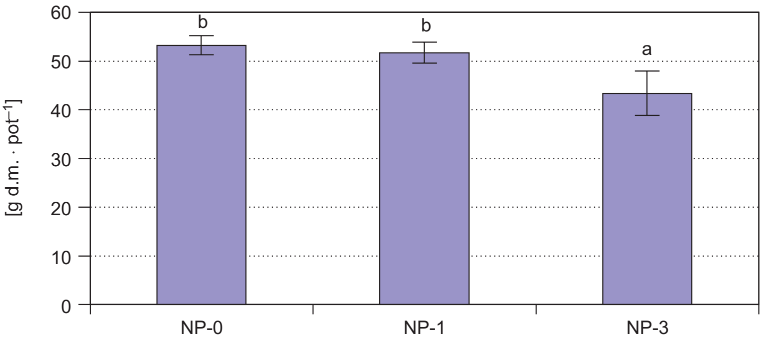

Fig. 1. The total amount of biomass oats and spring rape. Means followed by the same letters did not differ significantly at $\alpha \leq 0.05$ according to the t-Tuckey test

Independently of the amount of newspaper added to the soil, a decrease in weighted average amount of chromium, nickel and lead was noted in spring rape and oats aboveground parts in comparison with the content assessed in the aboveground parts of plants from the control (NP-0). It was observed that biomass of the aboveground parts of plants from the object which received 1 % newspaper supplement contained on average from 33 % to 53 % less of the analysed trace elements. On the other hand, a 3 % admixture of newspaper to the soil contributed to a decline in weighted average content of chromium, nickel and lead even by 63 % (Table 2).

Research conducted by Domanska [14] evidenced that plant aboveground parts contain much smaller amounts of nickel than roots. On the other hand, Antonkiewicz and Jasiewicz [15] observed that nickel is a relatively mobile element, easily absorbed by plants, whereas its translocation to the aboveground plant parts is greatly impeded. On the other hand, Gambus [16] thinks that the relationship of this type is conditioned by the properties of the plant itself. In case of nickel uptake by plants, also this element interactions with other trace elements, such as cadmium or zinc are crucial.

Table 2

Weighted mean cadmium, chromium, nickel and lead in the above-ground parts of spring rape and oats

Object	Cd	Cr	Ni	Pb
	[mg · kg^{-1} d.m.]			
NP-0	$0.70^{b} \pm 0.22$	$4.77^{b} \pm 1.21$	$4.50^{b} \pm 1.53$	$1.27^{a} \pm 0.37$
NP-1	$1.68^{a} \pm 0.13$	$2.73^{a} \pm 0.14$	$2.12^{a} \pm 0.03$	$0.85^{a} \pm 0.07$
NP-3	$1.55^{a} \pm 0.21$	$2.78^{a} \pm 0.37$	$1.68^{a} \pm 1.68$	$0.84^{a} \pm 0.18$

± standard deviation, n = 8; Means followed by the same letters in columns did not differ significantly at $\alpha \leq 0.05$ according to the t-Tuckey test.

An opposite relationship was registered for cadmium. Mean weighted content of this element in plants from the objects with newspaper waste supplement increased twice in comparison with the content noted in biomass from the control (NP-0). The differences were statistically significant.

Mean weighted average of chromium, nickel and lead assessed in the roots of rape and oats from the objects where newspaper supplement was added to the soil was smaller in comparison with these element concentrations determined in plant roots from the control (NP-0). Mean weighted average content of chromium in roots diminished by 56 % on NP-1 object and by 26 % on NP-3 object. For nickel the decrease was respectively 36 % (NP-1) and 6 % (NP-3) and for lead 42 % (NP-1) and 6 % (NP-3) in comparison with the control (NP-0). For cadmium content in plant roots (like in aboveground parts) an increase in its content was registered in the biomass from the objects which received a newspaper supplement. The increase for NP-1 object was 22 % and for NP-3 – 18 %. Irrespective of the analysed element, the assessed content generally did not differ statistically (Table 3).

Table 3

Weighted mean cadmium, chromium, nickel and lead in the roots of spring rape and oats

Object	Cd	Cr	Ni	Pb
	[mg · kg^{-1} d.m.]			
NP-0	$2.34^{a} \pm 0.99$	$17.35^{b} \pm 1.81$	$9.57^{a} \pm 1.22$	$6.97^{a} \pm 5.22$
NP-1	$2.85^{a} \pm 0.06$	$11.12^{a} \pm 0.85$	$7.06^{a} \pm 0.34$	$5.14^{a} \pm 1.06$
NP-3	$2.77^{a} \pm 0.34$	$13.82^{ab} \pm 2.91$	$9.06^{a} \pm 1.62$	$4.02^{a} \pm 0.52$

± standard deviation, n = 8; Means followed by the same letters in columns did not differ significantly at $\alpha \leq 0.05$ according to the t-Tuckey test.

According to Kabata-Pendias and Pendias [17], lead and chromium are elements little mobile in the soil environment. Research conducted by Lentynska-Synos [17] reveals that chromium uptake and transport in plants are connected mainly with iron presence. The amounts of cadmium absorbed by plants are directly proportional to this element content in the soil solution (irrespective of pH). Lentynska-Synos also thinks that cadmium is deposited mainly in roots and its natural content in plants is diversified depending on the species, as has been corroborated by the Author's own studies.

Chromium and nickel quantities absorbed by plant biomass in the objects with an admixture of newspaper to the soil were markedly smaller in comparison with these elements amount taken up by plants in the object where no newspaper was added. The experiment did not reveal any significant differences in the amounts of lead taken up by the plant biomass from individual objects. Total uptake of cadmium by spring rape and oats biomass from the objects with newspaper waste supplement was significantly higher than Cd quantities absorbed by plants in the control (Table 4).

Table 4

Total uptake of cadmium, chromium, nickel and lead with plants biomass

Object	Cd	Cr	Ni	Pb
	$[\mathrm{mg \cdot pot^{-1}}]$			
NP-0	$0.05^{a} \pm 0.02$	$0.34^{b} \pm 0.06$	$0.27^{b} \pm 0.27$	$0.11^{a} \pm 0.06$
NP-1	$0.09^{ab} \pm 0.01$	$0.19^{a} \pm 0.01$	$0.14^{a} \pm 0.14$	$0.07^{a} \pm 0.01$
NP-3	$0.07^{b} \pm 0.00$	$0.17^{a} \pm 0.17$	$0.11^{a} \pm 0.02$	$0.05^{a} \pm 0.01$

± standard deviation, n = 8; Means followed by the same letters in columns did not differ significantly at $\alpha \leq 0.05$ according to the t-Tuckey test.

Presented experiment has revealed that application of newspaper to the soil led to a decrease in its acidification (Table 5). In the object with 3 % newspaper supplement pH value increased by 10 % in comparison with pH value assessed in the soil material before the experiment outset.

Determined values of electrolytic conductivity for the soil with 1 % and 3 % additions of newspaper were $0.25 \mathrm{~mS \cdot cm^{-1}}$ and $0.38 \mathrm{~m \cdot cm^{-1}}$, respectively (Table 5). These values were higher than noted in the initial soil (Table 1) and in the soil from the control (NP-0) (Table 5).

Table 5

The values of pH and electrolytic conductivity in the soil
(mean of two years)

Object	pH KCl	Electrolytic conductivity $[\mathrm{mS \cdot cm^{-1}}]$
NP-0	$5.15^{a} \pm 0.03$	$0.05^{a} \pm 0.01$
NP-1	$5.79^{b} \pm 0.02$	$0.25^{c} \pm 0.03$
NP-3	$6.38^{c} \pm 0.18$	$0.38^{d} \pm 0.03$

± standard deviation, n = 8; Means followed by the same letters in columns did not differ significantly at $\alpha \leq 0.05$ according to the t-Tuckey test.

The effect of high value of electrolytic conductivity (regarded as the measure of soil salinity) is evidenced mainly as an impediment in water uptake [19]. The critical value of electrolytic conductivity impeding plant growth is regarded as the limit value of 1.0 mS · cm^{-1} [20]. Application of a bigger amount of newspaper waste to the soil contributed to its greater salinity, which in turn might have directly influenced a weaker plant development.

Investigations show that average for two years total contents of nickel, cadmium and lead in the soil in the objects where 1 % and 3 % newspaper supplement was added to the soil were lower in comparison to their concentrations assessed in the soil material from the control (NP-0). Cadmium content determined in NP-1 and NP-3 objects was twice lower in comparison with the amounts in the soil material from the object where no newspaper was added (NP-0) (Table 6).

Table 6

Mean content (of two years) of Cd, Cr, Ni and Pb in soil

Object	Cd	Cr	Ni	Pb
	[mg · kg^{-1} d.m.]			
NP-0	$0.83^{b} \pm 0.11$	$13.14^{ab} \pm 0.23$	$9.35^{a} \pm 0.31$	$24.97^{b} \pm 0.81$
NP-1	$0.47^{a} \pm 0.02$	$13.96^{b} \pm 0.70$	$9.13^{a} \pm 0.08$	$23.24^{a} \pm 0.34$
NP-3	$0.44^{a} \pm 0.01$	$12.68^{a} \pm 1.34$	$9.00^{a} \pm 0.19$	$22.74^{a} \pm 0.47$

± standard deviation, n = 8; Means followed by the same letters in columns did not differ significantly at $\alpha \le 0.05$ according to the t-Tuckey test.

Statistical analysis of the results confirmed the significance of differences. A much weaker effect of dilution was observed for nickel and lead. Nickel concentration after the application of 1 % and 3 % newspaper supplement in relation to soil material dry weight contributed to a decrease in nickel content in the soil material by 2.4 % in NP-1 object and 3.8 % in NP-3 object. The situation was similar for lead, where the decreases in this element content were 7.4 % and 9.1 %, respectively, in comparison with the control (NP-0). The exception was chromium of which 6.2 % higher concentration was assessed in NP-1 object.

Total content of trace elements in biodegradable waste materials, such as newspaper allows to determine their potential environmental applications [21]. The literature data confirm the relationship between total content of trace elements in soil and their concentrations in plants. On the other hand, the quantities of trace elements accumulated by plants depend on the rate of trace element translocation from the waste materials to the soil solution and also on the biomass amount.

Conclusions

1. Newspaper application to the soils did not lead to an increase (except for cadmium) in the contents of lead, chromium or nickel in plant aboveground parts.

2. Analysed trace elements were accumulated mainly in plant roots. In relation to the aboveground parts, the roots contained on average from 51 % to 82 % greater quantities of the studied elements.

3. A bigger supplement of newspaper (3 %) to the soil affected a greater accumulation of the analysed trace elements in the roots and lower in the plant aboveground parts.

4. Newspaper supplement to the soil caused lowering its acidification.

5. Application of newspaper to the soil generally did not affect the total content of analysed trace elements.

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OCENA ZAWARTOŚCI WYBRANYCH PIERWIASTKÓW ŚLADOWYCH W ROŚLINACH I W GLEBIE PO APLIKACJI PAPIERU GAZETOWEGO

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Abstrakt: Przeprowadzone badania miały na celu ocenę zawartości Cr, Cd, Ni i Pb w glebie oraz w biomasie roślin po aplikacji papieru gazetowego. Doświadczenie wazonowe prowadzono w latach 2010 i 2011 w hali wegetacyjnej. Doświadczenie obejmowało następujące obiekty: NP-0 – kontrola (gleba bez dodatku papieru gazetowego), NP-1 – gleba z 1 % dodatkiem papieru gazetowego oraz NP-3 – gleba z 3 % dodatkiem papieru gazetowego. Dodatek papieru gazetowego obliczono w stosunku do suchej masy materiału glebowego. Badania prowadzono w wazonach mieszczących 5,50 kg powietrznie suchego materiału glebowego. W doświadczeniu uprawiano dwie rośliny, w pierwszym roku rzepak jary odmiany 'Feliks', natomiast w drugim owies nagoziarnisty odmiany 'Siwek'. Rzepak jary zbierano w końcu fazy kwitnienia (73 dni wegetacji), a owies w fazie dojrzałości mlecznej (75 dni wegetacji). Po odpowiednim przygotowaniu materiału roślinnego i glebowego, zawartość badanych pierwiastków śladowych oznaczono metodą ICP-OES na aparacie Perkin Elmer Optima 7300DV, a uzyskane wyniki przeliczono na absolutnie suchą masę materiału. Doglebowa aplikacja papieru gazetowego nie spowodowała zwiększenia zawartości (za wyjątkiem kadmu) ołowiu, chromu i niklu w częściach nadziemnych roślin. Badane pierwiastki śladowe były gromadzone głównie w korzeniach roślin. W stosunku do części nadziemnych roślin korzenie zawierały średnio od 51 % do 82 % więcej badanych pierwiastków. Większy dodatek papieru gazetowego (3 %) do gleby skutkował większą akumulacją badanych pierwiastków śladowych w korzeniach, a mniejszą w częściach nadziemnych roślin. Dodatek papieru gazetowego do gleby spowodował zmniejszenie zakwaszenia. Wprowadzenie do gleby papieru gazetowego na ogół nie wpłynęło na zwiększenie ogólnej zawartości badanych pierwiastków śladowych.

Słowa kluczowe: papier gazetowy, gleba, rośliny, pierwiastki śladowe

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HABITAT CONDITIONS AND DIVERSITY OF FLORA BASED ON TRANSITIONAL PEAT BOG IN BLEDOW ON THE SILESIAN UPLAND

WARUNKI SIEDLISKOWE A ZRÓŻNICOWANIE ROŚLINNOŚCI NA PRZYKŁADZIE TORFOWISKA PRZEJŚCIOWEGO W BŁĘDOWIE (WYŻYNA ŚLĄSKA)

Abstract: Presented research focused on determining the characteristics of soils, waters and vegetation covering a transitional peat bog in Bledow and potential hazards which might cause its degradation. Four soil pits were made for this purpose and piezometers were installed in their immediate vicinity. It allowed investigation of physical and chemical properties of this habitat waters.

Diversity of the peat bog vegetation was determined on the basis of 17 phytosociological relevés made by Braun-Blanquet's method. The results demonstrated that the analysed peat bog is at the accumulation phase and the main factor shaping the habitat conditions in the peat bog itself and on its edge was high groundwater level. On the other hand, the feeding water and its level affected chemical and physical properties of the analysed peat bog soils. Low value of the studied peat bog water mineralisation and low share of calcium and magnesium ions in the mineralisation influenced low pH values and low degree of base cation saturation, which has been reflected in the floristic composition of the peat bog. In conditions of high moisture content, a process of organic matter accumulation was taking place in the surface horizons, whereas on the peat bog and on its edge an apparent soil and vegetation zonation was visible. On the edge of the peat bog trees encroaching into *Sphagno recurvi-Eriophoretum angustifolii* peat bog patches was observed on semi-hydrogenic soils and disappearance of species of the *Scheuchzerio-Caricetea nigrae* class. It was found that disturbance of natural water relationships poses the most serious potential hazard to the analysed peat bog.

Keywords: transitional peat bog, hydromorphic soils, Bledow

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Introduction

Hydrogenic and semihydrogenic habitats are the part of the natural environment to a great extent responsible for increasing biodiversity. Numerous rare and endangered animal [1] and plant [2] species, as well as mushrooms [3] under legal protection occur on wetlands. However, these are habitats largely susceptible to degradation and the balance may be easily disturbed even by a small lowering of groundwater level, eutrophication of hydrogenic oligotrophic habitats or in result of abandoning of the previous land use [4, 5].

One of such habitats in the western part of the Bledow Desert is transitional peat bog in Bledow. Despite the fact that it covers only about 0.2 ha, it is a key element of the natural environment in this area, increasing its biodiversity and being the habitat for many stenotypic plant and animal species [6]. Occurrence of these species and their forming plant communities is connected with specific habitat conditions.

The aim of the paper was a characterisation of soils, waters and vegetation covering the peat bog, but also determining potential hazards which might cause its degradation.

Materials and methods

The analysed peat bog is located on the Silesian Upland, in the eastern part of Bledow bogs in the Biala Przemsza River Valley (N 50° 20′ 22″, E 19° 27′ 05″). Four soil pits were made (profiles P1, P2, P3 and P4) to determine the properties of peat bog soil and soils situated on its edge. Samples for analyses were collected once from genetic horizons of the individual studied soils. Piezometers were installed in each place where a soil pit was made (PI, PII, PIII and PIV) to determine physical and chemical properties of the habitat waters. Water was sampled in March, May, July, September and November 2012. Because of a low groundwater level in the place where P1 pit was made, no water samples were collected from PI piezometer. The peat bog location was established using GPS technique.

The following assessments were made in the analysed soils: pH (by potentiometric method in H_2O and 1 mol · dm^{-3} KCl solution), mineral content (in organic horizons as weight loss at calcination at 550 ^{o}C), organic carbon and total nitrogen content on LECO CNS 2000 apparatus and sorption capacities [7]. The taxonomic classification of the studied peat bog soils was made on the basis of criteria in the Taxonomy of the Soils of Poland [8].

In the water samples collected from the investigated fens assessed were: oxygenation, mineralization, electrolytic conductivity and ionic composition, using the methods suggested by Dojlido [9].

In order to identify the diversity of the vegetation on the peat bog in Bledow, 17 phytosociological relevés were made by means of Braun-Blanquet method [10]. The relevés were distributed evenly over the whole area of the peat bog to obtain the vegetation picture. The names of communities and their syntaxonomical affiliation were based on [11], names of plant species are given in compliance with the paper by Mirek et al [12] and names of bryophytes after Ochyra et al [13].

Results and discussion

Among the natural environment elements affecting the habitat conditions one may mention geological substratum, high level of groundwater together with its chemical and physical properties [14]. The investigated peat bog formed in a depression with relative depth of about 2.5 m, on sandy substratum underlain with hardly permeable loam layer. Owing to this fact water affecting the trend of pedogenic processes and species composition of the vegetation accumulated in this concavity. On the other hand, high level of groundwater favoured the development of hydrogenic plant communities gradually passing into more dry peat bog edges.

The analysed peat bog is surrounded by fresh pine forest, developed on carbonateless initial soils – arenosols, characterised by very low groundwater level. Gleysols occur on the edges of the peat bog adjoining the forest; their bedrocks are carbonateless fluvioglacial sands, more deeply underlain with heavy loam or clay. Peat soils and patches of compact sphagnum moss mats formed in the most waterlogged central part of the peat bog.

Therefore the following vegetation zones may be identified on this peat bog:

– ecotonal (the peat bog edge) – between the peat bog and the forest, where overgrowing with trees and bushes patches of *Sphagno recurvi-Eriophoretum angustifolii* alliance formed on ground-gley soils occur (profile P1),

– bog plant formations (peat bog) – *Sphagno recurvi-Eriophoretum angustifolii* on peat fibrous-heme soils,

– mat of *Rhynchosporetum albae* and *Caricetum limosae* sphagnum mosses forming flowing layers of compact sphagnum moss mats (fibrous soils), (profiles P3 and P4).

The properties of hydrogenic habitat soils are associated with a number of factors among which the most important are chemical and physical properties of the mineral substratum on which these habitats are formed, the type of hydrological water feeding, its oxygenation and ionic composition. These factors affect the species composition of the flora settling hydrogenic habitats [4, 5, 15].

The investigated peat bog developed on a carbonateless substratum, however the type of its hydrological feeding cannot be determined unanimously. The more so, as its location in the vicinity of the Biala Przemsza River causes that during high water stages, the river water may feed the peat bog. Undoubtedly, precipitations also play a crucial role, moreover the share in the feeding of surface runoffs flowing into in the concavity should not be disregarded, either. The above mentioned agents variously influence the ionic composition of the feeding waters. A lack of carbonates in the substratum in place of peat bog formation and low mineral content, including calcium and magnesium ions, in the feeding waters affected low pH values of the studied soils and their sorption properties. It concerns among others low base saturation (Table 1). Similar relationships in mezotrophic mountain fen soils were described by Nicia and Niemyska-Lukaszuk [16].

Waters feeding the peat bog reveal low mineralization (Table 2). On the basis of minerals content, water collected in the piezometers may be classified, after Macioszczyk [17], to ultra-sweet waters with mineralization below 100 mg $\cdot$ dm^{-3}. Despite this, diversified

Table 1

Physical and chemical properties of the studied soils

Thickness of the horizon	Horizon	Ash	pH		C_{org}	N_{tot}	C/N	Sorption properties							
								Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	S	K_h	CEC*	BS**
			KCl	H_2O	$[g \cdot kg^{-1}]$			$[mmol(+) \cdot kg^{-1}]$							[%]
Profile P1															
0–6	Ol	36.5	4.7	3.6	368.5	7.9	47	75.5	18.7	10.5	1.9	106.6	676.5	783.1	13.6
6–12	Oa	66.3	4.8	3.8	195.3	4.5	43	46.7	6.9	3.7	0.9	58.1	364.0	422.1	13.8
12–26	AG	—	5.2	4.4	2.6	0.3	9	5.4	0.4	0.1	0.3	6.2	25.7	32.0	19.5
> 26	G	—	5.3	4.8	1.2	0.1	12	3.4	0.3	0.1	0.1	3.9	14.7	18.6	21.0
Profile P2															
0–17	Oi	61.5	4.7	3.5	223.6	5.9	38	214.3	23.4	11.7	3.1	252.4	757.4	1009.7	25.0
17–35	Oie	67.3	4.8	4.2	189.7	5.2	36	215.6	23.7	1.5	2.1	242.9	595.6	838.5	29.0
35–107	C	—	5.4	4.8	0.7	0.1	7	4.7	0.4	0.1	0.2	5.3	12.9	18.2	29.3
Profile P3															
0–10	O1i	13.6	4.5	3.6	501.2	8.9	45	5.2	1.2	1.4	1.9	9.6	415.6	425.2	2.3
10–50	O2i	38.3	4.6	3.8	358.1	8.1	38	3.2	1.3	1.6	2.1	8.1	405.2	413.3	2.0
Profile P4															
0–9	O1i	14.2	4.4	3.8	497.4	8.5	42	6.2	1.3	1.4	1.7	10.6	412.5	423.1	2.5
9–45	O2i	40.2	4.5	3.9	346.9	8.2	35	3.7	1.3	1.1	1.4	7.6	398.3	405.9	1.9

* CEC – cation exchange capacity; ** BS – base saturation.

mineralization was noted among the samples collected from individual piezometers. Water collected from piezometer PII installed in peat soil of the transitory peat bog was characterized by the highest content of minerals, whereas almost twice lower was assessed in waters collected from piezometers PIII and PIV.

Table 2

Properties of studied groundwater

Property* ± SD**				
Piezometer		PII	PIII	PIV
Temperature	^{o}C	11.1*± 5.1**	12.5 ± 6.4	12.6 ± 6.4
pH	—	5.6 ± 1.0	4.9 ± 0.8	4.9 ± 1.1
Conductivity	[$\mu S \cdot cm^{-1}$]	66.1 ± 33.1	47.3 ± 19.3	45.4 ± 20.1
Mineralization	[$mg \cdot dm^{-3}$]	52.2 ± 24.8	35.6 ± 14.5	34.0 ± 15.1
O_2		0.6 ± 0.3	0.5 ± 0.3	0.6 ± 0.4
HCO_3^-		12.1 ± 8.7	8.9 ± 4.6	9.4 ± 6.7
SO_4^{2-}		18.3 ± 4.6	10.0 ± 4.2	8.8 ± 4.0
Cl^-		1.6 ± 1.5	0.5 ± 0.3	0.4 ± 0.3
NO_3^-		6.0 ± 2.8	5.6 ± 3.0	5.4 ± 1.9
NH_4^+		0.1 ± 0.1	0.1 ± 0.1	0.1 ± 0.1
PO_4^{3-}		0.2 ± 0.1	0.2 ± 0.1	0.2 ± 0.1
Ca^{2+}		5.5 ± 2.4	4.4 ± 2.2	3.1 ± 1.9
Mg^{2+}		1.5 ± 0.9	1.0 ± 0.6	0.9 ± 0.4
Na^+		2.4 ± 1.9	1.2 ± 0.6	1.3 ± 0.5
K^+		4.5 ± 1.8	3.7 ± 1.3	4.4 ± 1.3

* Means for the investigated period; ** SD – standard deviation.

Higher content of calcium and magnesium ions and higher mineralization of the peat bog waters (piezometer PII) in comparison with the waters collected from the compact mat of sphagnum moss (piezometers PIII and PIV) affected chemical properties of the analyzed soils. Soil samples collected from the peat bog were characterized by higher pH values, higher cation exchange capacity and higher share of calcium and magnesium ions in the sorption complex in comparison with the samples taken from the compact mat of sphagnum moss.

Basing on the Priklonski-Szczukariew classification [17] waters of the central peat bog part (P2) may counted among the four-ion waters of the 39th class, *ie* bicarbonate-sulphate-magnesium-calcium waters. On the other hand, a lower proportion of magnesium in the ionic composition of the water from compact mat of sphagnum moss (P3 and P4) allowed to classify them to three-ion waters, of the 18th class, *ie* bicarbonate-sulphate-calcium waters. Higher values of total mineralization and higher contents of calcium and magnesium ions in the ionic composition of the peat bog waters may be explained by their enrichment in minerals from the substratum on which the peat bog was formed. Wolanin and Zelazny [18] described similar relationships in mountain spring waters, whereas Nicia and Miechowka [19] in waters feeding hydrogenic habitats.

Gleying process encompassing lower parts of the soil profile was going on in the soils of the peat bog edge, on which *Sphagno recurvi-Eriophoretum angustifolii* phytocenoses, overgrowing with birch and pine trees formed. Because groundwater in the peat bog edge occasionally reached only 0.15–0.25 m from the soil level, during a major part of the period of investigations, no water was found in piezometer P1. On the other hand, organic matter accumulated in the top layers of these soils. Despite high moisture content, it should not be associated with organic matter accumulation process, but rather with the deposition of needles and leaves from the trees growing on these patches. The matter occurred as forest litter. The soils on the outer part of the peat bog edge were characterized by a lower groundwater level and lower thickness of organic horizons in comparison with the soils located closer to the central part of the peat bog.

Higher than in the peat bog edge groundwater level in the soil of the central peat bog part favoured development of vegetation typical for wetlands and represented by *Sphagno recurvi-Eriophoretum angustifolii* phytocenoses. Apart from *Eriphorum angustifolium*, which is the species dominant in the structure of these patches, also *Viola palustris*, *Agrostis canina*, *Carex echinata* and *Comarum palustre* played a crucial role, as well as representatives of the *Oxycocco-Sphagnetea* class: *Drosera rotundifolia* and *Andromeda polifolia*. Sphagnum moss blankets were formed mostly from *Sphagnum fallax* and *Sphagnum teres*. In conditions of high groundwater level, dead peat bog plant remnants were deposited as partly decomposed organic matter, but high groundwater level in the central part of the peat bog slowed down organic matter decomposition process. Surface horizons in the central part of the peat bog and of the compact mat of sphagnum moss in anaerobic conditions caused by high groundwater level were characterised by a low degree of organic matter decomposition (H_{2-3} acc. to von Post scale) [8]. The thickness of organic horizon was increasing gradually towards the central part of the peat bog with lowering depth of mineral substratum. In the central part of the peat bog in places where the mineral substratum lay at the depth of over 1.5 m, patches of *Sphagno recurvi-Eriophoretum angustifolii* vegetation were gradually passing into *Rhynchosporetum albae* and in the most waterlogged places in *Caricetum limosae* phytocenoses. These phytocenoses formed dense mats of sphagnum moss, between 0.5 to 1.0 m thick gradually overgrowing a water filled cavity in which the peat bog developed.

Rhynchosporetum albae occured in complex with *Caricetum limosae* and S*phagno recurvi-Eriophorertum angustifolii* phytocenoses in slightly more dry places than *Caricetum limosae* phytocenoses. Still, these habitats were characterised by high moisture content. The dominant species, determining the character of the discussed alliance patches was *Rhynchospora alba*, accompanied by among others: *Eriophorum angustifolium*, *Menyanthes trifoliate* and *Carex limosa*. The permanent components of this phytocenosis included also: *Oxycoccus palustris* and *Drosera rotundifolia*. On the other hand, *Sphagnum palustre*, *S. flexuosum* and *S. fallax*. were present in the moss layer.

The most precious components of this peat bog vegetation were well developed patches of *Caricetum limosae*, observed in the central, lowered part of the peat bog in strongly waterlogged places where water was always stagnating. The moss layer was poorly developed and did not exceed 40 %. On the other hand the appearance of the discussed patches is shaped by *Carex limosa* – the species under legal protection [2] which also belongs to extinct flora species, not only in the Silesia region [20], but throughout Poland [21]. *Carex limosa* was accompanied by plants from *Scheuchzero-Caricetea nigrae* class – mainly *Menyanthes trifoliata*, *Comarum palustre* and *Eriophorum angustifolium*. Also a small share of species typical for wet meadows and bulrushes.

Beside *Carex limosa*, also other protected species occurred in the species composition of vegetation covering the studied peat bog (Table 3).

Table 3

Share of protected species in the investigated phytocenoses

Caricetum limosae	*Rhynchosporetum albae*	*Sphago recurvi-Eriophoretum angustifolii*
Carex limosa	*Utricularia intermedia*	*Drosera rotundifolia*
Menyanthes triforiata	*Drosera anglica*	*Menyanthes trifoliata*
Drosera rotundifolia	*Drosera rotundifolia*	*Pedicularis palustris*
	Carex limosa	*Dactylorhiza incarnata*
	Menyanthes trifoliata	*Ledum palustre*

The floristic values and phytecenotic diversity of this peat bog as an object worth of protection have been already emphasized in the subject literature [6, 22]. The investigations demonstrated that the peat bog values remain very high, the more so, as the habitat with the code 7140, which occurs here, represented by transitory peat bogs and quagmire (prevalently with *Scheuchzerio-Caricetea nigrae* vegetation is a habitat protected by the European legislation (Habitat Directive 92/43/EWG) and very rare in the region).

Conclusions

1. High groundwater level was the factor to the greatest extent shaping the habitat conditions, influencing the vegetation and the trend of pedogenic processes both in the ecotone zone between the studied peat bog and pine forest, and in the peat bog itself.
2. Low value of water mineralization, its small share of calcium and magnesium ions influenced low pH values and base saturation in the soils of the peat bog itself and its edge.
3. Lowering of groundwater level on the peat bog edge favoured occurrence of trees and bushes in the patches of S*phagno recurvi-Eriophorertum angustifolii* formation but disappearance of the species from *Scheuchzerio-Caricetea nigrae* class.
4. High groundwater level favours organic matter accumulation in the peat bog. However, changes in water relationships in this area may cause disturbances of dynamic equilibrium and lead to extinction of many stenotypic, legally protected plant species from this area.

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WARUNKI SIEDLISKOWE A ZRÓŻNICOWANIE ROŚLINNOŚCI NA PRZYKŁADZIE TORFOWISKA PRZEJŚCIOWEGO W BŁĘDOWIE (WYŻYNA ŚLĄSKA)

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Abstrakt: Badania dotyczyły określenia charakterystyki gleb, wód oraz roślinności porastającej torfowisko przejściowe w miejscowości Błędów oraz potencjalnych zagrożeń, mogących spowodować jego degradację. W tym celu wykonano 4 odkrywki glebowe, a w ich bezpośrednim sąsiedztwie zainstalowano piezometry. Umożliwiło to zbadanie właściwości fizycznych i chemicznych wód tego siedliska.

Zróżnicowanie roślinności torfowiska określono na podstawie 17 zdjęć fitosocjologicznych wykonanych metodą Braun-Blanqueta. Wyniki badań dowiodły, że badane torfowisko znajduje się w fazie akumulacji, a głównym czynnikiem kształtującym warunki siedliskowe w samym torfowisku, jak i jego okrajku był wysoki poziom wód gruntowych. Z kolei woda zasilająca oraz jej poziom kształtowały właściwości chemiczne i fizyczne gleb badanego torfowiska. Niska wartość mineralizacji wód badanego torfowiska oraz mały udział w mineralizacji jonów wapnia i magnezu były przyczyną małych wartości pH oraz niskiego stopnia wysycenia kompleksu sorpcyjnego badanych gleb kationami o charakterze zasadowym, co znajduje odzwierciedlenie w składzie florystycznym torfowiska. W warunkach dużego uwilgotnienia w poziomach powierzchniowych zachodził proces akumulacji materii organicznej, a na torfowisku oraz jego okrajku stwierdzono wyraźną strefowość gleb i roślinności. W okrajkach torfowiska, na glebach semihydrogenicznych obserwowano wkraczanie drzew i krzewów w płaty mszaru S*phagno recurvi-Eriophorertum angustifolii* i zanikanie gatunków klasy *Scheuchzerio-Caricetea nigrae.* Stwierdzono, że największe potencjalne zagrożenie badanego torfowiska stanowi naruszenie naturalnych stosunków wodnych.

Słowa kluczowe: torfowiska przejściowe, gleby hydrogeniczne, Błędów

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INFLUENCE OF GRANULATING FACTOR AT VARIABLE HUMIDITY ON GRANULATION OF PARTIALLY ACIDULATED PHOSPHATE ROCKS

WPŁYW CZYNNIKA GRANULUJĄCEGO PRZY ZMIENNEJ WILGOTNOŚCI NA GRANULACJĘ FOSFORYTÓW CZĘŚCIOWO ROZŁOŻONYCH

Abstract: Unstable situation on fertilizer raw material market emerges the need to find substitute for superphosphate fertilizers. PAPR-type phosphate fertilizers (partially acidulated phosphate rock) constitute the most relevant alternative. PAPR-type fertilizers are formed by reaction of phosphate rock with nonstoichiometric, in relation to reaction during superphosphate production process, portion of mineral acid. The resulting product contains an available (soluble in water and/or in neutral ammonium citrate) and less available (soluble in mineral acids) forms of phosphorus. Possibility of using low-grade phosphate rock represents a great advantage of PAPR-type over superphosphatic manufacturing process, where applying phosphate rock of high P_2O_5 at low impurities content is highly recommended. Granulation process is an essential stage of PAPR-type fertilizers production. Granulation significantly reduces the dust emissions during the fertilizers application furthermore limits the regression of fertilizers in soil to unavailable forms (so-called the aging processes of fertilizers). Optimization of process parameters is very important for economic and ecological reasons because this process is one of the most energy consuming in whole cycle of PAPR-type fertilizers production. PAPR-type fertilizer preparations obtained under laboratory conditions were subjected to examinations. Products were characterized by a variable humidity, which was achieved by altering the concentration of mineral acid used for investigations. The second variable factor was the type of liquid used for granulation. Both, the sieve analysis and determination of resistance were carried out for classification of obtained granules.

Keywords: fertilizers, granulation, partially acidulated phosphate rock

Phosphorus, next to nitrogen and potassium, is one of the plant essential macronutrients, that is why phosphate fertilizers are an indispensable part of agriculture, and

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their consumption in Poland in the 2009/2010 season amounted to about 35 million tons [1]. The main product of phosphate fertilizers industry branch is superphosphate, applied as a straight primary nutrient fertilizer or as an intermediate used in the production of compound primary nutrient fertilizers. Phosphate rock constitutes a basic raw material used for the production of superphosphate. For several years there has been considerable fluctuations in phosphorus commodity prices. Currently, the price of phosphate rock is twice higher than as about 5 years ago and reaches approximately 180 USD per ton [2]. The primary requirement for phosphate raw materials destined to produce superphosphate is high P_2O_5 with low impurities content at the same time [3, 4]. Deposits of phosphate rock with high content of P_2O_5 are available only in deposits located in a few countries in the world. The greatest resources are in Morocco, China, USA and Russia [1]. Poland has only a few small low-grade deposits, however their extraction is economically unreasonable due to too low concentration of phosphate rock in relation to the entire deposit [5]. Therefore Polish industry of phosphate fertilizers is based on imported raw materials. Possibility of increasing the independence of the phosphorus raw material is one of the main reasons for finding alternatives for conventional superphoshate fertilizers. Poland in 2008 was placed on the 5th place in the EU in terms of consumption of mineral fertilizers (100–150 kg/ha). Moreover Poland was also their significant producer (approximately 1.5 % of world production) [1]. This is another significant reason for becoming the issues, connected with development of technology designed for production of phosphate fertilizers based on low-grade phosphate rock, a priority for Polish phosphate fertlizers industry.

One of the existing alternatives for the production of conventional superphosphate fertilizers is based on partial acidulation of phosphate rocks, so called PAPR-type fertilizers (partially acidulated phosphate rock). The main advantage of PAPR-type fertilizer is economics of the manufacturing process by taking into consideration the fact that their production can be performed using phosphate rock with P_2O_5 content below 20 % w/w [4]. The amount of deposits of low-grade and low-quality phosphate rocks is considerably higher worldwide as reserves of high-grade and high-quality phosphate rock are being depleted. It may cause a significant reduction in the cost of raw material required for fertilizer manufacturing processes. PAPR-type fertilizers are produced as a consequence of the following total reaction (1) [6]:

$$3Ca_3(PO_4)_2 \cdot CaF_2 + 7H_2SO_4 \longrightarrow 7CaSO_4 + 3Ca(H_2PO_4)_2 + 2HF \qquad (1)$$

Superphosphate manufacturing process is based on the same reaction, however the PAPR-type fertilizer process involve less amount of mineral acid than it results from the stoichiometry of the process, which is furthermore important taking into consideration environmental aspects. As a consequence of reduced amount of mineral acid, obtained fertilizer formulation contains both forms of phosphorus: water-soluble and soluble in neutral ammonium citrate (*ie* forms easily absorbed by plants) as well as the forms of phosphorus soluble in mineral acids (forms rather insoluble and thus unavailable to plants). The insoluble forms of phosphorus constitute a phosphorus stock in the soil, which can be transformed in the available form by the microbial metabolic processes occurring in the soil [7].

Granulation is an unit operation by means of fertilizer product alter its form and significantly improves its mechanical properties. The granular form cause increase in bulk density what both reduces the space required for storage and transportation costs. Moreover it significantly facilitates the regular fertilizer dosing on agricultural land [8, 9]. The use of granules reduces dust during packaging and application of fertilizers, which significantly reduces the harmful effects of the production process and applications on the environment. In the case of phosphate fertilizers very important advantage of using granular form is the limitation of precipitation processes which cause reversible transformation from the available phosphorus forms to mineral forms which are insoluble for plants (so-called aging of fertilizers), because of the fact that these processes occur only on the surface of the granules whereas available forms of phosphorus are being regularly released from within the granule (reaction 2–4) [10].

$$Ca(H_2PO_4)_2 + 2Al(OH)_3 \longrightarrow 2Al(OH)_2 \cdot H_2PO_4 + Ca(OH)_2 \tag{2}$$

$$Ca(H_2PO_4)_2 + Ca(HCO_3)_2 \longrightarrow CaHPO_4 + 2H_2CO_3 \tag{3}$$

$$2CaHPO_4 + Ca(HCO_3)_2 \longrightarrow Ca_3(PO_4)_2 + 2H_2CO_3 \tag{4}$$

As a result of the granulation process the product is characterized by homogeneous composition which allows regular supply of macro- and micronutrients into the soil [9]. The most relevant disadvantage of granulation process constitutes significant increase in production costs, it may be as high as 30 % [8, 9]. Granulation can be carried out using diversified methods, however the pug-mill, drum and pan granulators are selected for the most part by phosphate fertilizer manufacturers [9]. The required size of the granules for phosphate fertilizers is 1–6 mm [8, 11].

Materials and methods

The aim of the experiment was to determine dependence of the type of granulating liquid and the moisture content of samples on the quality of resulting granules. Production parameters subjected to modifications were:

– the type of granulating liquid (water and sulfuric acid (H_2SO_4) 5 % w/w solution);

– moisture content of the fertilizer formulation (2.5 %, 5.0 %, 7.5 % and 10 % w/w H_2O);

– the degree of PAPR stoichiometric norm (η_{PAPR}= 0.3; 0.5; 0.7; where η_{PAPR} defines the proportion of the quantity of mineral acid used in the process to the quantity of acid, which results from the stoichiometric reaction of phosphate rock acidulation).

Phosphate rock used in this investigation was provided from the phosphate deposits located in west part of the Nagev desert in Israel. The study consisted in granules formulation in laboratory conditions, sieve analysis of the obtained product and performing the test of mechanical strength of granules. Acidulation process for fertilizer products was conducted in modular batch reactor Atlas (Syrris Ltd.) equipped with a reaction vessel made from teflon introduced into an aluminum heating jacket, possessing the ability to control the process parameters such as temperature, stirring intensity and reaction time automatically from the main panel. In order to obtain the fertilizer product, each time a weighed portion of phosphate rock (50 g) was stirred with the amount of acid suitable in accordance with the assumed values of PAPR stoichiometric norms as well as established moisture content of the sample. After completion of the acidulation reaction in the reactor 15 g of the PAPR product was subsequently subjected to granulation process. Granulation was carried out in a laboratory-scale granulator using elements of the drum and pan granulators. Granulator is made of tube containing two rings, which serve as mechanical barriers for granular material, which facilitated the agglomeration of particles of the fertilizer. However, in contrast to the standard drum granulators is opened only on one side, causing further agglomeration of particles at the bottom of the granulator, which is a feature of the pan granulation. The resulting granules were subjected to drying at 105 °C for 6 hours. After the drying process and adjusting temperature to room conditions granules were then sieved and analyzed in scope of separation of the desired fraction (1–6 mm). Then, the desired fraction was tested for crushing strength of granules using the ERWEKA® device in order to evaluate the mechanical strength. The obtained granules were compared with granules based on powder superphosphate fertilizer provided by one of the leading manufacturers of phosphate fertilizers. In addition results of the strength of lab-derived PAPR-type fertilizers granules were related to the strength of granulated fertilizers available on the Polish market.

Results

Figure 1 shows the results of sieve analysis for a PAPR-type product of $\eta_{PAPR} = 0.5$ where water was used as a granulating liquid. Figure 2 shows the mechanical strength test results of granules obtained for the same product.

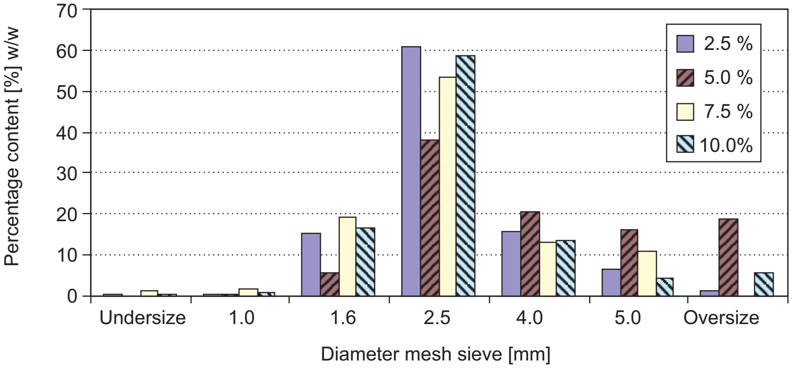

Fig. 1. The results of sieve analysis of a sample granulated by H_2O ($\eta_{PAPR} = 0.5$)

Granule size distribution for all levels of moisture contents in the examined samples was identified by the highest values for medium-mesh sieve which means that the size distribution is close to normal distribution.

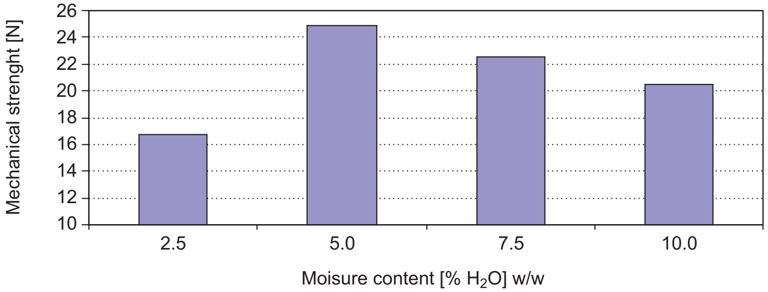

Fig. 2. The results of mechanical strength analysis for granules obtained from the PAPR fertilizer product of $\eta_{PAPR} = 0.5$ granulated by H_2O

The highest compressive strength was achieved for moisture content equal to 5.0 % w/w. of H_2O. It should be noted that the sample of the following moisture content was characterized by the highest share of granules with a diameter greater than 4 mm, which can cause increase in the value of the granules mechanical strength.

Figure 3 shows the results of sieve analysis for a PAPR-type product of $\eta_{PAPR} = 0.3$ where H_2SO_4 5.0 % w/w solution was used as a granulating liquid. Figure 4 shows the mechanical strength test results of granules obtained for the same product.

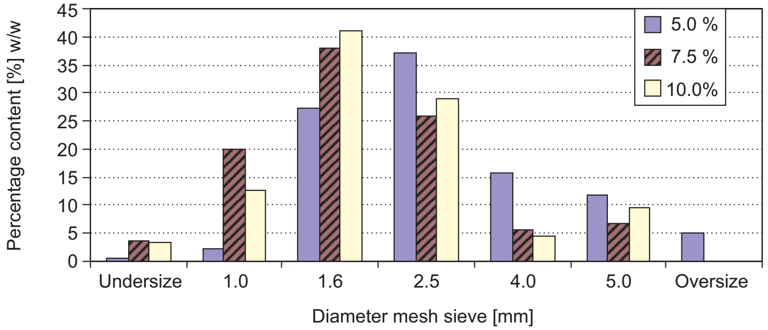

Fig. 3. The results of sieve analysis of a sample granulated by H_2SO_4 solution ($\eta_{PAPR} = 0.3$)

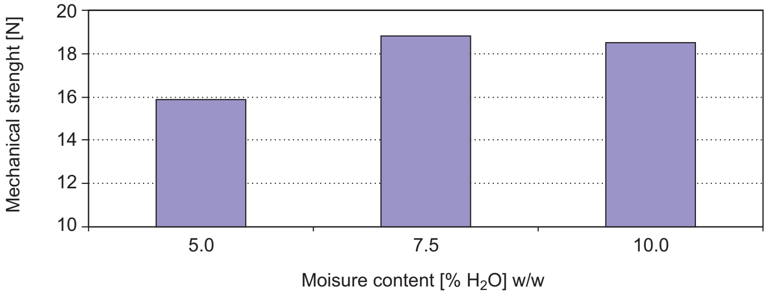

Fig. 4. The results of mechanical strength analysis for granules obtained from the PAPR fertilizer product of $\eta_{PAPR} = 0.3$ granulated by H_2SO_4 solution

Granule size distribution for the following moisture contents 7.5 % w/w H_2O and 10.0 % w/w H_2O in obtained samples revealed a trend for smaller mesh sizes which turns this distribution to the left-oblique approach. However, for the moisture content of 5.0 % w/w H_2O granule size distribution is slightly shifted to the right.

The highest compressive strength was achieved for moisture content equal to 5.0 % w/w of H_2O despite the fact that part of the granules with a diameter greater than 4 mm for this sample was the lowest among the tested samples.

Figure 5 summarizes the results of mechanical strength analysis for all formulations obtained during the investigations.

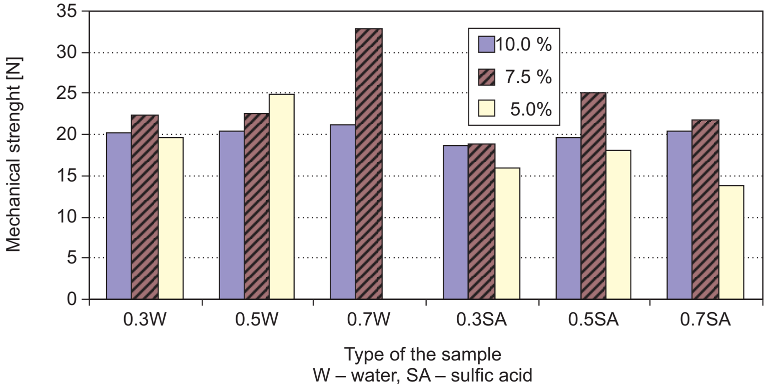

Fig. 5. Comparison of the results of mechanical strength analysis for granules obtained on the basis of all investigated products. The number indicates the degree of the applied value of PAPR stoichiometric norms (*eg* 0.3 means $\eta_{PAPR} = 0.3$), whereas granulating liquids are marked as follows: W – water; SA – sulfuric acid solution

The results indicates clearly that the sample of moisture content at 7.5 % w/w H_2O is characterized by the highest mechanical strength. It is relevant to point out that for the majority of applied values of degree of PAPR stoichiometric norms the lowest values of mechanical strength were found for samples of moisture content at 5.0 % w/w H_2O. The optimum moisture content for granular samples comprises between 7.5 and 10.0 % w/w H_2O. The results of analysis presented in this paper does not allow to select certain granulating liquid, which could improve mechanical properties of the granules in a significant degree.

Figure 6 depicts the comparison of results of mechanical strength analysis for selected products obtained during the investigations commercial products available on the market.

For the majority of applied values of degree of PAPR stoichiometric norms the highest strength was recorded for samples of moisture content at 7.5 % w/w H_2O. It was also verified that the highest mechanical strength of granules occurs for samples in which the size distribution of granules during sieve analysis is shifted to the right, towards the larger diameter of the granules. However, these results in increase in the amount of oversized particles which in turn generates the necessity to transfer oversized

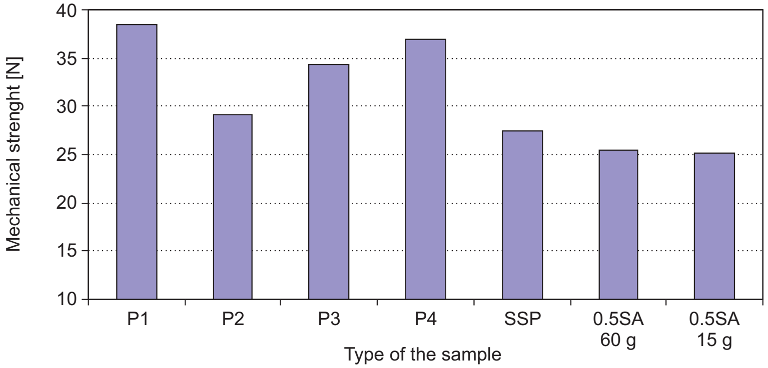

Fig. 6. Comparison of mechanical strength of granules. P1:P4 – granular fertilizers available on the Polish market; SSP – granules obtained on the basis of investigated method using superphosphate provided by one of the Polish manufacturers; 0.5SA 60 g – granules obtained on the basis of PAPR product $\eta_{PAPR} = 0.5$ granulated with a solution of sulfuric acid and weight of the sample at 6 g; 0.5SA 15 g – granules obtained on the basis of PAPR product $\eta_{PAPR} = 0.5$ granulated with a solution of sulfuric acid and weight of the sample at 15 g

granules into crushing unit and turning them back to the process. The best properties are achieved when granules size distribution is close as possible to normally distributed (sufficient strength and a small amount of undersized and oversized granules). Commercial products were characterized by a higher mechanical strength of granules, however it is worth noting that industrial granulators have a much larger diameter resulting in a much larger forces that affect the particles during the granulation process. This was confirmed by the result of single superphosphate granulation by method used to obtain investigated PAPR formulations. The mechanical strength of the superphosphate granules was similar to the strength of the other granules obtained on the basis of PAPR fertilizers.

Conclusions

The research indicated the possibility to obtain a ready PAPR product of proper quality at reduced influence of the curing process, which may reduce the time required for fertilizer manufacturing and unit production costs. The most promising results were obtained for the PAPR-type formulations of a moisture content at 7.5 % w/w. Further studies on this issue should be conducted for a sample with a moisture content at 7.5 % w/w or close to this value. Any significant difference in the quality of the PAPR fertilizer products obtained on the basis of different granulating liquid was found, what allows to draw a conclusion that there is no need for a specific granulating liquid that could raise production costs. Further investigations on this issue should focus on determining the quality of granules depending on such factors as the angle of the granulator, the number of rate per minute and feeding conditions of granulating liquid.

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WPŁYW CZYNNIKA GRANULUJĄCEGO PRZY ZMIENNEJ WILGOTNOŚCI NA GRANULACJĘ FOSFORYTÓW CZĘŚCIOWO ROZŁOŻONYCH

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Abstrakt: Niestabilna sytuacja na rynku surowców nawozowych stwarza konieczność znalezienia substytutu dla nawozów superfosfatowych. Najważniejszą alternatywą wydają się być nawozy fosforowe typu PAPR (*partially acidulated phosphate rock*). Nawozy typu PAPR powstają w wyniku reakcji fosforytów z niestechiometryczną, względem reakcji produkcji superfosfatów, ilością kwasu. Tak powstały produkt zawiera formy fosforu zarówno łatwo przyswajalne (rozpuszczalne w wodzie i/lub w obojętnym cytrynianie amonu), jak i nieprzyswajalne (rozpuszczalne tylko w kwasach mineralnych) przez rośliny. Zaletą tego rodzaju nawozów jest fakt, że do ich produkcji można wykorzystać fosforyty o znacznie mniejszej zawartości P_2O_5 niż jest to wymagane dla procesu produkcji nawozów superfosfatowych. Proces granulacji jest niezbędnym elementem procesu otrzymywania nawozów typu PAPR ponieważ znacznie zmniejsza emisję pyłów w czasie stosowania nawozów, dodatkowo granulacja nawozów fosforowych znacznie ogranicza uwstecznianie się nawozów do form nieprzyswajalnych (tzw. procesy starzenia się nawozów) w glebie. Optymalizacja parametrów procesu granulacji jest bardzo istotna ze względów ekonomicznych oraz ekologicznych, ponieważ proces ten jest jednym z najbardziej energochłonnych w całym cyklu produkcji nawozów. Do badań wykorzystano preparaty nawozów fosforowych typu PAPR otrzymane w laboratorium. Otrzymane preparaty charakteryzowały się zmienną wilgotnością, co osiągnięto poprzez zmianę stężenia kwasu użytego do reakcji. Drugim zmiennym czynnikiem był rodzaj cieczy użytej do procesu granulacji nawozów typu PAPR. W celu klasyfikacji otrzymanych granulatów przeprowadzono analizę sitową oraz oznaczono wytrzymałość otrzymanych preparatów.

Słowa kluczowe: nawozy, granulacja, częściowo rozłożone fosforyty

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IMPACT OF ANTHROPOPRESSURE ON MEADOW AND GROVE PEDOFAUNA IN LANDSCAPE PARK IN KRAKOW-ZAKRZOWEK

WPŁYW ANTROPOPRESJI NA PEDOFAUNĘ ŁĄKI I ZAGAJNIKA W PARKU KRAJOBRAZOWYM W KRAKOWIE ZAKRZÓWKU

Abstract: The consequence of accumulation of heavy metals (that can be detected in trace content in natural conditions) in soil is biological deactivation of environment manifesting in limitation of processes of organic substances decomposition by decreasing density, diversity and activity of the microorganisms and pedofauna.

In order to evaluate the impact of pollution of environment by heavy metals a few chosen physiochemical parameters of meadow and grove soil in Landscape Park were detected.

It was noted that soil of researched areas had slightly alkaline reaction, whereas concentration of Cd, Pb and Zn was higher in young pine forest soil, however only concentration of Cd in both areas was above the norm. In the soil of the meadow considerably higher density and diversity of groups of pedofauna analyzed was detected. In 1 m^2 of meadow soil 4928 specimen were noted, while 3264 in forest soil. In the meadow *Diptera* larvae was the most diverse group, since within its order 10 families were isolated. In forest soil specimen of 4 *Diptera* larvae families were noted. Trophic relations of dipterofaunal larvae communities biomass significantly differ from a model designed for natural meadows.

Keywords: pedofauna, density, diversity, heavy metal, *Diptera* larvae

The soil animals, due to their various relations, are very important factors in the soil formation processes, mineralization, but also in the humification of the dead organic matter. As a result of their search for the nutrition the survival and vegetative forms of bacteria and fungi spread mainly in the form of the undigested leftovers of nutrition of the soil animals. In that way, the microorganisms can settle on the new deposits of the organic matter. The fragmentation and mixing by the soil invertebrates of the organic

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matter coming to the soil is extremely important, because it makes the organic matter available for the microorganisms [1, 2]. Due to its mobility, the pedofauna (mainly meso- and macrofauna) influences as well the aggregate structure of the soil and the size of the pores and tubules. Therefore, in this way the pedofauna determinates the absorption, maintenance and storage of the water by the soil. This capacity of the pedofauna explains the fact that many researchers call it "soil engineer". It is claimed that the matter coming to the soil passes through the alimentary canal of the soil animals at least once and that their excrements constitutes almost the entire level of the soil humus [3]. Soil fauna represents the large number of species, which play an important role in different ecosystem functions, such as the transfer of organic matter in soil or soil structure dynamics [4, 5].

The number of pedofauna specimen in m^2 of the meadow soil can reach around 260 mln (among them about 200 mln are Protozoa) with the biomass around 150 g d.m. among which the most dominant group is microfauna [6]. The number of the meso- and macrofauna is lower and can even reach 54000, whereas the biomass of meso and macrofauna is similar to those of microfauna [7]. Macrofauna are one of animals groups that occur in litter and soil in big numbers, especially big biomass, high diversity and different trophic relations. In temperate beech forest there may be as many as a 1000 species of animals, among which 200 species of arthropods in 1 m^2 of soil [8]. In the average soil of the various land ecosystems around 150 *Lumbricidae* in 1 m^2 was detected, whereas the density of the remaining macrofauna (the most of *Coleoptera* larvae and other *Insecta*, imagines *Formicidae* included , as well as *Aranea*) can reach a few hundred in 1 m^2. The density of mesofauna that is *Collembola*, *Acarina and* small *Diptera* larvae can reach several dozen thousands [3, 7]. Because of the fact that similar groups of invertebrates appear in various types of the soils in great numbers and that the borders of the groups are clearly defined, the pedofauna is frequently used in the researches on the impact of pollutions on the soils [8–10]. Monitoring studies using bioindicators provide information on the assessment of environmental pollution, the spread of contaminants and their bioavailability. Mechanisms of penetration of the analytes and the influence of abiotic factors on their accumulation in the structures of sorption in indicator organisms have not yet been sufficiently identified [11]. The various human activities influence the quality of the ecosystems, causing, for example, the changes in density, biomass, size as well as species and genetic diversity within pedofauna. Many researchers report the drastic reduction of the number and diversity of species within pedofauna as a result of the use of the pesticides and the contamination of the soil by the heavy metals [10, 12]. Soil contamination of heavy metals can have dramatic effects on soil invertebrates and therefore can lead to significant changes in the functioning of the soil [13]. It was indicated, that the most sensible to the pollutions are the *Oligochaeta* and the larvae of the most insects, because the humid surface of their bodies enables the diffusion of the pollutions, dissolved in the soil solution, to their tissues.

The consequence of the accumulation of the heavy metals in the soil (that can be detected in trace content in natural conditions) is the biological deactivation of the environment. This process is manifested, among others, in the limitations of the organic matter decomposition processes because of the reduction of the density, diversity and activity of the microorganisms and pedofauna.

In this perspective, the evaluation of the changes in the density, biomass and diversity of these animals, caused by the various human activities is an essential task. For the level of predators the highest concentration of toxic pollutants is available. Therefore the trophic structures of density and biomass of *Diptera* larvae communities, with particular attention to analysis of the predators were examined. The structure was compared with another trophic structure of biomass of *Diptera* larvae groups typical for the areas with low emission of pollutions [14].

Materials and methods

In order to evaluate the impact of the anthropopressure on the soil subsystem a few chosen physiochemical and biological parameters, that were: soil moisture [%] and pH of the soil, density and diversity of meso- and macrofauna, density and biomass as well as diversity within the *Diptera* larvae in the meadow and grove soil in the Landscape Park were detected. On the area of the Bielansko Tyniecki Landscape Park 2 types of habitats were chosen:

1. The meadow in Krakow-Zakrzowek;
2. The pine grove-around 40-year old situated near the meadow, but lower and nearer to the traffic lane.

With the use of Morris square frame (25 cm by 25 cm) a series of samples was taken on the selected sites during autumn 2008. The frame was thrust into the soil on the depth of 10 cm. In each particular site a series consisted of 16 tests on the surface of 1 m^2. Invertebrates were scampered away by employing the dynamic method in the modified Tullgren apparatus. After marking select meso- and macrofauna its density and diversity were analyzed in detail. Soil moisture and its pH and temperature as well as the content of Pb, Zn, Cd, Cu, were determined owing to the method FAAS (AAS firmy Cole-Parmer, BUCK 200A).

Diptera larvae biomass was determined by measuring their length, then the rate based on Schatz [15] and Petersen & Luxton [16] was applied. *Diptera* larvae trophic relations were indicated on the basis of Gobat et al and Brauns [17, 18].

Results and discussion

It was noted that soil of researched areas had slightly alkaline reaction, because their pH was from 7.38 to 7.78 (Table 1). Since only the low pH increases the assimilability of the heavy metals (mainly Pb and Cd) by the soil organisms, the reaction was not the increaser of the metals mobility in the researched areas [19, 20].

The soil moisture [%] of the meadow soil was on average around 8 % higher than the grove soil. It indicates that, in this case, the soil moisture causes the changes in the density and diversity of the group of pedofauna analyzed (Table 1).

Table 1

General characteristics of soil and pedofauna

Parameter	Grove	Meadow
Number meso- macrofauna [sp. N/m^2]	3264	4928
Diversity (number of taxonomic group)	17	19
Diversity *Diptera* larvae (number of families)	4	11
Biomass *Diptera* larvae [mg/m^2 d.m.]	14.77	398.33
Soil pH	7.65 (7.56–7.74)	7.57 (7.36–7.78)
Soil moisture [%]	20.95 (20.2–21.7)	28.55 (25.2–31.9)

The differences in Cd, Pb, Zn and Cu content were noted as well. In the grove soil the number of Cd, Pb and Zn was higher than in the meadow soil, whereas the number of Cu was higher in the meadow soil (Fig. 1). As the research indicates, only the number of Cd in both habitats was above the norm- that is 1 mg/kg d.m. [21]. However, in the meadow the number of Cd was slightly less than two times above the norm (1.9 mg/kg d.m.), whereas in the grove almost two and a half times higher (2.3 mg/kg d.m.).

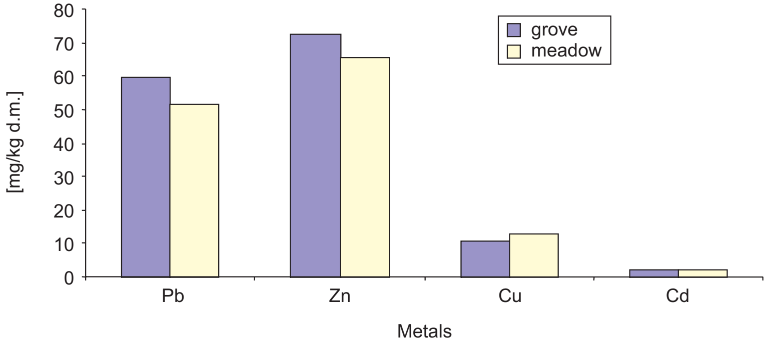

Fig. 1. Concentration of heavy metals in soil of areas analyzed [mg/kg d.m.]

Cd and Pb are the elements strongly influencing the environment, qualities of the soils and plants and health of people and animals [22]. As the research concerning fauna indicates, the considerable pollution of the soil by Cu and Pb leads to the changes in the soil qualities, biological among others [8, 9]. In the habitats analyzed, apart from the changes in the density and diversity of the meso- and macrofauna, the changes within *Diptera* larvae groups were noted as well (Table 2 and 3).

The content of the metals analyzed in the chosen habitats correlated with the number and diversity of the fauna analyzed. In the meadow soil the lower concentration of Cd, Pb and Zn was noted in comparison to the grove soil. What is more, in 1 m^2 of the meadow soil the highest density (4928 specimen) of the animals analyzed was detected. Also in the meadow soil the highest diversity of meso- and macrofauna was noted

Table 2

Density [sp. no./m^2] and indicator of domination [%] of pedofauna

Taxonomic group	Grove		Meadow	
	[sp. N/m^2]	[%]	[sp. N/m^2]	[%]
Lumbricidae	8	0.25	16	0.32
Symphyla	24	0.74		
Lithobius sp.	56	1.72	48	0.97
Geophilus sp.	48	1.47	24	0.49
Julus sp.	16	0.49		
***Coleoptera imago*:**				
Staphylinidae	8	0.25	40	0.81
Carabidae			8	0.16
Ptilidae	40	1.22		
Coleoptera larvae	72	2.21	40	0.81
Thysanoptera	56	1.72	8	0.16
Gastropoda			8	0.16
Isopoda	16	0.49	8	0.16
Diptera imago	16	0.49	16	0.32
Diptera larvae	32	0.98	**200**	4.06
Hymenoptera imago:				
Formicidae	32	0.98	56	1.14
Collembola	**1200**	**36.76**	**1920**	**38.96**
Pseudoscorpionidae	16	0.49		
Protura	24	0.74	16	0.32
Aranea			8	0.16
Acarina	**1552**	**47.55**	**2456**	**49.84**
Lepidoptera imago			8	0.16
Lepidoptera larvae			32	0.65
Dermoptera			16	0.32
Homoptera larvae	48	1.47		
Sum total	3264		4928	

(Table 2). The researches concerning *Diptera* larvae confirm clearly the results. *Diptera* larvae were analyzed in detail taking into consideration the number of the various families within their groups, and their density and biomass. The higher diversity, density and biomass of larvae in comparison to the grove soil were detected in the meadow soil (Table 3).

Moreover, according to the indicator of domination the part of *Diptera* larvae was bigger in the groups of the meadow pedofauna (Table 3). *Diptera* larvae are character-

Table 3

Density and biomass of *Diptera* larvae

Familie Name	Trophic group	Grove		Meadow	
		[N/m^2]	[mg/m^2 d.m.]	[N/m^2]	[mg/m^2 d.m.]
Cecidomyiidae	Ph	8	2.11	32	10.56
Chironomidae	S			16	7.39
Limoniidae	P			16	17.39
Syrphidae	Ph			8	4.22
Dolichopodidae	P	8	4.22	16	9.5
Ceratopogonidae	S	8	4.22	40	17.95
Phryneidae	S			8	6.34
Stratiomyiidae	S			8	89.76
Tipulidae	Ph			16	40.92
Lonchaeidae	S	8	4.22	40	194.30
Sum total		32	14.77	200	398.33

S – Saprophag; P – Predator; Ph – Phytophag; [density] = N/m^2; [biomass] = mg/m^2 d.m.

ized by wide morphological, ecological and behavioral diversity. They may use different food resources offered by the soil. Trophic relations of dipterofaunal communities were also analyzed (Fig. 2) and were compared with the model designed for natural meadows by Ciesielska [14].

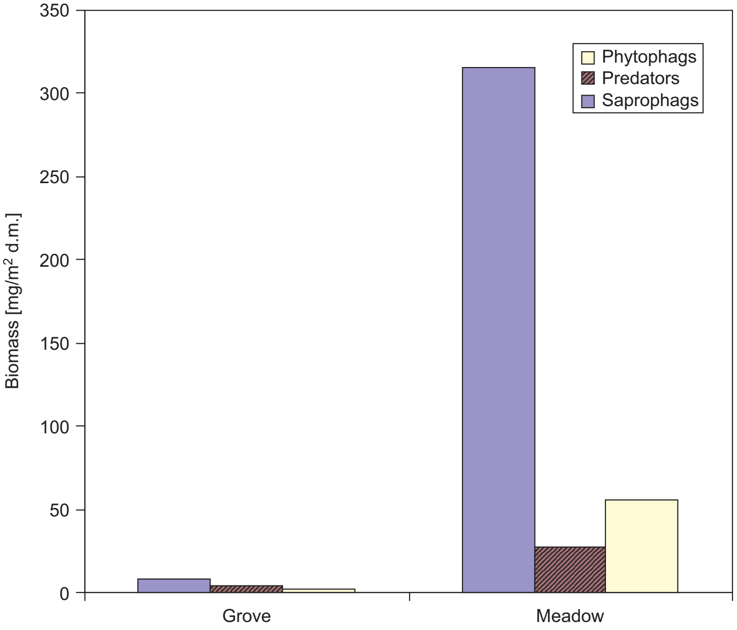

Fig. 2. Trophic relations of *Diptera* larvae communities biomass

Trophic relations of dipterofaunal larvae communities biomass significantly differ from a model. These differences depend on very small participation of saprophags against phytophags and predators, and may point at disturbances in the soil subsystem on studied localities caused by anthropogenic pressure. At the same time very high biomass of predators and saprophags larvae in the meadow shows smaller human impact than in the grove.

Dusts emitted by the non-ferrous foundries, carbon burning and traffic pollutions are the main sources of the spot and area pollutions of the soils by the heavy metals. The amount of the pollutions emitted by the motor vehicles apart from the size of the traffic intensity is determined mainly by the distance from the road and landform features. The danger increases accordingly to the traffic intensity and is generally limited to the width of 150–200 m at each side of the road [23]. In the conducted research, apart from the industry and carbon burning, the traffic is one of the main sources of the pollutions. The traffic is probably one of the sources of the higher concentration of Cd, Pb and Zn in the grove soil – situated lower than the meadow and nearer to the busy Tyniecka street.

Conclusions

In the grove soil the content of Cd, Pb and Zn was higher than in the meadow soil, whereas the content of Cu was higher in the meadow soil.

The content of heavy metals in the chosen habitats correlated with the number and diversity of the soil fauna.

The higher diversity, density of pedofauna and biomass of *Diptera* larvae in comparison to the grove soil were detected in the meadow soil.

Trophic relations of dipterofaunal larvae communities biomass may point at disturbances in the soil subsystem on studied localities caused by anthropogenic pressure.

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WPŁYW ANTROPOPRESJI NA PEDOFAUNĘ ŁĄKI I ZAGAJNIKA W PARKU KRAJOBRAZOWYM W KRAKOWIE ZAKRZÓWKU

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Abstrakt: Konsekwencją kumulacji metali ciężkich w glebie (występujących w warunkach naturalnych w ilościach śladowych) jest dezaktywacja biologiczna środowiska przejawiająca się m.in. ograniczeniem procesów rozkładu substancji organicznych poprzez zmniejszenie zagęszczenia, różnorodności i aktywności mikroorganizmów oraz pedofauny.

W celu oceny wpływu zanieczyszczenia środowiska metalami ciężkimi zbadano wybrane parametry fizykochemiczne w glebie zagajnika i łąki w Parku Krajobrazowym w Zakrzówku.

Stwierdzono, że gleba badanych siedlisk wykazywały odczyn lekko zasadowy, natomiast stężenie Cd, Pb i Zn było wyższe w glebie młodego zagajnika sosnowego, ale tylko w przypadku kadmu w obydwu siedliskach przekraczało normę. W glebie łąki wykryto znacznie większą liczebność i różnorodność pedofauny. W 1 m^2 gleby łąkowej odnotowano 4928 osobniki, a w glebie leśnej 3264. Na łące larwy *Diptera* były najbardziej zróżnicowaną grupą, bowiem w ich obrębie wyodrębniono przedstawicieli 10 rodzin. W glebie leśnej odnotowano tylko 4 rodziny larw *Diptera*. Struktura troficzna larw *Diptera* w biomasie znacznie różni się od modelu stwierdzonego dla naturalnych łąk.

Słowa kluczowe: pedofauna, zagęszczenie, różnorodność, metale ciężkie, larwy *Diptera*

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PERVAPORATION MEMBRANE CONTAINING IONIC LIQUID FOR BIOBUTANOL CONCENTRATION

PERWAPORACYJNA MEMBRANA Z DODATKIEM CIECZY JONOWEJ DO ZATĘŻANIA BIOBUTANOLU

Abstract: The paper describes the creation process for an active layer of pervaporation membrane containing ionic liquid achieved by its appropriate blending with PDMS and hardening by way of polycondensation. The test was performed with the use of hydrophobic ionic liquids with butanol selectivity – 1-butyl-3methyl-imidazolium bis (trifluoromethylsulfonyl) imide and 1-hexyl-3-methylimidazilium hexafluorophosphate. The influence of mass content of components and the type of supporting layer on the membrane process parameters was analyzed. Then the prepared membranes were tested in pervaporation process of biobutanol concentration from the model quaternary solution of acetone-butanol-ethanol-water. The process was carried out continuously in a steady state conditions. The permeate side pressure was 30 mbar, feed temperature was 50 ^{o}C and the feed flow rate was 40 dm^3/h. Compositions of permeate and retentate were analyzed using gas chromatography.

Preparation of membranes obtained by polycondensation hardening of the solution consisting of ionic liquid and PDMS enabled us to provide the most appropriate membranes for pervaporation process. The observed permeate fluxes were at relatively low levels due to additional resistance caused by the thickness of PDMS layer.

Keywords: membrane, ionic liquid, pervaporation, biobutanol

Biobutanol is a modern fuel and alternative source of energy. As its properties are similar to petrol, it can be used as petrol additive for internal combustion engines. Relatively low heat of vaporization is one of its advantages as it facilitates engine start up at low temperatures. It is less susceptible to separation from petrol in the presence of water than ethanol. Moreover, it contains less oxygen per mass unit and thus can be added to petrol at higher volumes. Typical blends of ethanol with petrol contain 5–20 % of ethanol, while blends with butanol contain 8–32 % of butanol.

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Biobutanol is obtained mainly by way of biomass fermentation which results in the acetone-butanol-ethanol aqueous solution (ABE fermentation) with the 3:6:1 mass ratio. Typical raw materials include sugar cane, corn or wheat but other cellulose containing materials, such as wood waste could also be used, which would greatly decrease the cost of biobutanol production. As a result of ABE fermentation butanol of the concentration of up to 3 wt. % is obtained. Isolation of the product from fermentation broth constitutes a serious technological issue as traditional distillation is not profitable.

Studies indicate that the modern membrane technology of pervaporation (PV) can be utilized for isolation of butanol from the broth. Pervaporation is a separation technique which involves phase change of the first type combined with mass transfer across nonporous composite membrane, which allows for separation and concentration of the product within a single process. In the case of ABE post-fermentation product, the organic fraction: butanol, acetone and ethanol are transported across the hydrophobic membrane. Literature provides examples of studies about *n*-butanol separation and recovery from aqueous solutions by PV with the use of both, commercially available and independently manufactured silicone membranes [1–4]. Contemporary scientific research indicates possibility of incorporation of ionic liquids, which are selective for butanol, into pervaporation membranes.

Ionic liquids (ILs) for that application are liquids in room temperature and consist of ions only. They usually consist of a large, asymmetrical cation and a wide range of anions which influence melting point of the compound, depending on their structure and composition.

Ionic liquids are called designer solvents which means that their properties can be adjusted to match the requirements of a given process [5]. The key factors in separation of mixtures are low volatility and high incidence in liquid state (often above 200 ^{o}C) [6] which enables their easy regeneration and recirculation to the process. Low solubility in aqueous solutions of the ionic liquid used as extraction solvent is crucial for separation of biobutanol.

There are some methods for use ILs as an active separation layer in membranes. The first approach is the linking of polymerisable groups to the IL molecules and the direct crosslinking of the ILs by covalent bonding. In this case, membrane exhibits different permeation behaviour than without ILs [7]. The second approach represents ion exchange membranes where anions or cations of ILs might be immmobilised in membrane material. In another approach ILs can be solidified by use of gelling agents [8, 9]. Gelators allow to obtain high IL contents, but show low chemical and mechanical stability limit their suitability for pervaporation. In related approach, ILs are often solidified by dissolving these liquids in a polymer. In the literature, some polymers using to this method preparation has been reported, *eg* polyvinyl alcohol (PVA), polyvinyl chloride (PCV), poly(dimethyl siloxane) (PDMS), poly(ether block amide) (PEBA) [10, 11]. In this paper the last method creation of pervaporation membrane was used. The membranes were achieved by appropriate blending ionic liquid with PDMS and hardening it by polycondensation.

Materials

Pervaporation membranes were formed with the use of commercially available, two component liquid silicone rubber (POLSIL Solar) hardened at room temperature to a transparent rubber with Solar catalyst, made by Chemical Plant “Polish Silicones” Ltd). 1-hexyl-3-methylimidazolium hexafluorophosphate [Hmim][PF_6] and 1-butyl-3-methylimidazolium bis(trifluoromethylsulphonyl)imide [Bmim][Tf_2N] (see Figure 1 for chemical structure) obtained from IoLiTec (Ionic Liquid Technologies, Germany) were used as ionic liquids with low water solubility and affinity for butanol [12, 13]. Acetone, ethanol and *n*-butanol (POCh) were used for pervaporation tests.

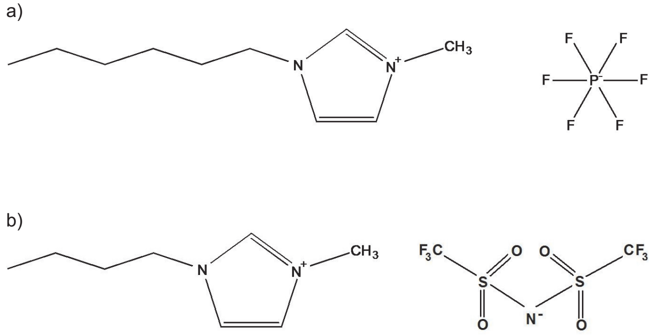

Fig. 1. Structural formula a) 1-hexyl-3-methylimidazolium hexafluorophosphate; b) 1-butyl-3-methylimidazolium bis(trifluoromethylsulphonyl)imide

Flat pervaporation membranes were obtained by blending POLSIL Solar solution with a suitable ionic liquid and adding Solar catalyst. Then the solution was gently stirred and deaerated. Such solution was poured onto supporting layer of the membrane. Two types of supporting layers were used: parchment paper for food packing (39 g/m^2) covered with a layer of silicone (0.5 g/m^2) and nylon net pulled over a flat glass surface used to overcome resistance of flow of the layer. This solution poured over the supporting layer of the membrane was equally distributed all over the surface. The solution was subject to polycondensation hardening at room temperature within 48 hours. Thickness of membranes obtained was between 150 and 200 μm and was controlled with the amount of poured solution. The process of pervaporation was performed with the use of 160 mm discs prepared directly on parchment paper used as supporting layer as well as discs cut out from a sheet poured over nylon net.

Test methods

Obtained membranes were used for pervaporation tests of biobutanol concentration using Sulzer Chemtech laboratory apparatus. The feed consisted of aqueous solution of three organic components, acetone-butanol-ethanol with the 3 : 6 : 1 mass ratio, just as the broth after ABE fermentation. All tests were performed with fixed feed composition amounting to 3 wt. % of butanol to enable comparison of quality of obtained membranes. The process was carried out continuously in a steady state conditions. The permeate side pressure was 3 kPa, feed temperature was 50 °C and the feed flow rate was 40 dm^3/h [14]. Chemical constitution of permeate and retentate was analyzed by gas chromatography using ThermoFinnigan apparatus and BTR-CW column. To measure the concentration, the sample was additionally diluted with 5 % aqueous methanol solution that was at the same time used as the internal standard.

Based on the experiments, permeate weight and mole fractions of individual components in the permeate (x_{ip}) were obtained. The data obtained was used to calculate total permeate flux and partial permeate fluxes (J_{tot}, J_i [$kg/(m^2h)$] as well as membrane diffusion coefficients for individual components (D_i [m^2/h]). These parameters define membrane selectivity and enable comparison of pervaporation results for various membranes.

Diffusion coefficient was calculated with the use of partial permeate flux formula. The driving force behind the process of pervaporation is the difference in activity:

$$J_j = \rho_i \frac{D_i}{\delta} \Delta a_i \quad \left[\frac{\mathrm{kg}}{\mathrm{m^2 h}}\right] \tag{1}$$

where: ρ_i – density of component i at operating temperature [kg/m^3],
δ – membrane thickness [m],
Δa_i – difference in activity of component i in permeate and feed [-] calculated with the following formula:

$$\Delta a_i = \gamma_{ip}\, x_{ip} - \gamma_{iF}\, x_{iF} \quad [-] \tag{2}$$

where: γ_{iP}, γ_{iF} – activity coefficient of component i in the permeate and feed [-].

Activity coefficients of individual components (γ_i) in the liquid for the quaternary solution – acetone-butanol-ethanol-water – at atmospheric pressure (feed pressure) and reduced pressure (permeate pressure) were determined with the use of NRTL equation (Non-Random Two-Liquid) as defined in the following formula (3).

$$\ln \gamma_i = \frac{\sum_{j=1}^{n} \tau_{ij}\, x_j\, G_{ji}}{\sum_{k=1}^{n} x_k\, G_{ki}} + \sum_{j=1}^{n} \frac{x_j\, G_{ij}}{\sum_{k=1}^{n} x_k\, G_{kj}} \left[\tau_{ij} - \frac{\sum_{m=1}^{n} \tau_{mj}\, x_m\, G_{mj}}{\sum_{k=1}^{n} x_k\, G_{kj}} \right] \tag{3}$$

where: $G_{ij} = \exp(-\sigma_{ij}\, \tau_{ij})$;
$\tau_{ij} = a_{ij} + b_{ij}/T + e_{ij} \ln T + f_{ij}\, T$;
$\sigma_{ij} = c_{ij} + d_{ij}(\mathrm{T}\text{-}273{,}15\ \mathrm{K})$;
T – temperature [K].

Calculations of activity coefficients (γ_i) for individual components were performed with the use of a dedicated MATLAB program [15], on the basis of pairs of coefficients for binary solutions. Calculations of τ and G intermediate constant values used in the equation (3) for the temperature of 323.15 K are shown in Tables 1 and 2.

Table 1

Values of τ constant at the temperature of 323.15 K generated with the use of MATLAB program and used to determine activity coefficients

τ [-]	Acetone	Butanol	Ethanol	Water
Acetone	0	0.635	0.292	0.8
Butanol	0.0038	0	0.398	0.323
Ethanol	0.404	0.264	0	0.039
Water	1.354	2.778	1.644	0

Table 2

Values of *G* constant at the temperature of 323.15 K generated with the use of MATLAB program and used to determine activity coefficients

G [-]	Acetone	Butanol	Ethanol	Water
Acetone	1	0.826	0.916	0.787
Butanol	0.999	1	0.888	0.908
Ethanol	0.886	1.082	1	1.012
Water	0.066	0.435	0.611	1

Test results

Preliminary crosslinking tests of POLSIL solution with an addition of ionic liquid for catalyst amounts of 6, 8, 10 and 20 wt. % were performed. No significant influence of used amounts of catalyst on the hardening rate of the solution within the period of analysis was observed. For this reason the amount of 8 wt. % in proportion to pure solution was used, as recommended by the manufacturer.

Then examinations of POLSIL solution miscibility with ionic liquids at 25 ^{o}C were performed. Both silicone rubber and the ionic liquids are viscous solutions with different density, which results in forming of two phases after blending and setting aside for some time. In order to determine the largest possible amount of ionic liquid that can be added to active membrane layer without observing visible separation of its phases, samples of solutions in the scope of 0.1–0.6 wt. fraction of ionic liquid in the solution were prepared. Samples were set aside to enable formation of crosslinking. Then homogeneity of their structures was analyzed. Samples with high fractions of ionic liquid showed condensation and joining of droplets into larger aggregates. Apparently, 36.5 wt. % (30 % of volume) is the limit amount of 1-hexyl-3-methylimidazolium hexafluorophosphate [Hmim][PF_6] that can be added to the solution. In case of 1-butyl-3-methylimidazolium bis(trifluoromethylsulphonyl)imide [Bmim][Tf_2N] 33 wt. % (25.8 % of volume) is the limit amount. Based on the above tests, membranes with limit amount of ionic liquid were able to be formed and their efficiency in comparison with pure silicon could be evaluated.

Figure 2 presents microscopic images of pure PDMS membrane made on a nylon net support and membrane with limit amount of ionic liquid [Hmim][PF_6] showing low transparency and visible condensation of ionic liquid in the membrane.

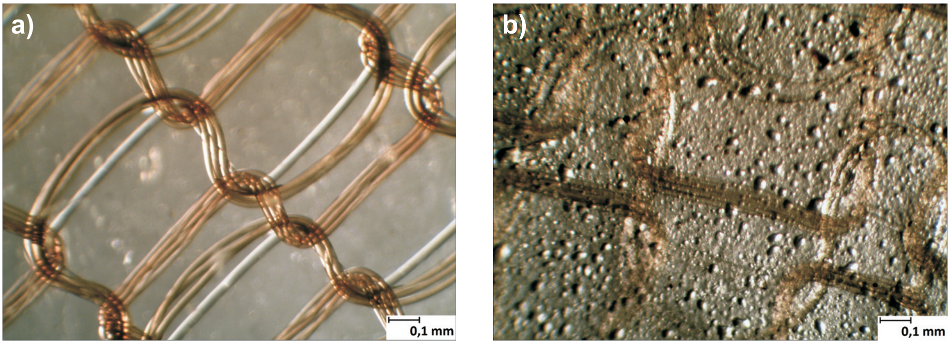

Fig. 2. Microscopic images of membranes: a) pure PDMS; b) 36.5 wt. % [Hmim][PF_6]

Initial tests of pervaporation separation for quaternary solution were performed on membranes immobilized on parchment paper with 0 wt. % and 25 wt. % amounts of ionic liquid. Distinct concentration of feed components was observed in neither case. Additionally low permeate fluxes indicated considerable membrane flow resistance. For this very reason parchment paper was replaced by a thin nylon net to be used as supporting layer in order to reinforce active layer of membrane and avoid additional resistance of flow. The thickness of membrane on the net was approximately 200 μm.

Further tests of pervaporation separation for the solution were performed on membranes with the nylon net. Diffusion coefficients for individual components were calculated for the tested membranes (Table 3).

Table 3

Pervaporation process parameters: permeate flux (J_{tot}) and diffusion coefficient of the selected component (D_i) for selected membranes with suitable mass content of ionic liquid (w)

No.	w [wt. %]	$D_{(Acet)}$ [m^2/h]	$D_{(BuOH)}$ [m^2/h]	$D_{(EtOH)}$ [m^2/h]	$D_{(H_2O)}$ [m^2/h]	J_{tot} [$kg/(m^2h)$]
1	0	$1.37 \cdot 10^{-8}$	$1.73 \cdot 10^{-8}$	$4.15 \cdot 10^{-8}$	$5.15 \cdot 10^{-8}$	0.054
2	25 [Hmim][PF_6]	$1.72 \cdot 10^{-8}$	$2.32 \cdot 10^{-8}$	$4.39 \cdot 10^{-8}$	$6.39 \cdot 10^{-8}$	0.075
3	36.5 [Hmim][PF_6]	$1.78 \cdot 10^{-8}$	$1.91 \cdot 10^{-8}$	$3.11 \cdot 10^{-8}$	$9.11 \cdot 10^{-8}$	0.080
4	33 [Bmim][Tf_2N]	$2.46 \cdot 10^{-8}$	$3.08 \cdot 10^{-8}$	$1.05 \cdot 10^{-7}$	$8.82 \cdot 10^{-8}$	0.107

Table 3 presents similar values of diffusion coefficients for all components. In all cases the values are higher for membranes with ionic liquid in comparison to pure PDMS membrane. Permeate fluxes were very low and reached the values from 0.054 to

0.1 kg/(m^2h). For comparison, pervaporation concentration performed with the use of commercially available PERVAP 4060 membrane for the same feed composition resulted in the flux of about 1.2 kg/(m^2h) [16]. The value suggests that thickness of active membrane layer was inadequate. Higher values of flux for membranes with ionic liquid compared with pure PDMS membrane may result from leaching of the liquid from membrane pores during the process, which was described in some papers [17, 18]. Therefore, it seems appropriate to create some additional layer to close ionic liquid within the membrane or change the method of PV membrane preparation.

Summary and conclusions

Membrane is the most important element of the PV process. It determines the separation of aqueous and organic phase. In this work membranes were obtained by polycondensation hardening of the solution consisting of ionic liquid and PDMS. Then the membranes were tested in pervaporation process. The diffusion coefficients and permeate fluxes were calculated.

The diffusion coefficients for all components trough PDMS membrane are of the same order. They are higher for membranes with ionic liquid in comparison to pure PDMS membrane. The ionic liquid enhances the diffusion of all components through the membrane.

During testing of the prepared membranes with different supporting layer it was found that resistance to mass transfer is mainly connected with the thickness of its active layer. It is advisable to form thinner PDMS layers. It directly contributes to increasing the permeate flux. It was observed higher values of flux for membranes with ionic liquid compared with pure PDMS membrane.

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PERWAPORACYJNA MEMBRANA Z DODATKIEM CIECZY JONOWEJ DO ZATĘŻANIA BIOBUTANOLU

Wydział Inżynierii Procesowej i Ochrony Środowiska
Politechnika Łódzka

Abstrakt: W pracy wytworzono warstwę aktywną membrany perwaporacyjnej z dodatkiem cieczy jonowej poprzez odpowiednie zmieszanie z PDMS i polikondensacyjne utwardzenie. Do badań użyto hydrofobowych cieczy jonowych: 1-butyl-3methylimidazolium bis (trifluoromethylsulfonyl) imide oraz 1-hexyl-3-methylimidazilium hexafluorophosphate, które wykazują selektywność w stosunku do butanolu. Przeanalizowano wpływ udziału masowego składników oraz rodzaj warstwy podporowej na parametry procesowe membrany. Na wytworzonych membranach wykonano badania perwaporacyjnego zatężania biobutanolu z modelowego czteroskładnikowego układu aceton-butanol-etanol-woda. Proces prowadzony był w sposób ciągły, w warunkach ustalonych, z ciśnieniem po stronie permeatu wynoszącym 30 mbar, w temperaturze 50 ^{o}C i z natężeniem przepływu nadawy 40 dm^3/h. Skład permeatu i retentatu był analizowany za pomocą chromatografii gazowej.

Szeroka preparatyka membran otrzymanych metodą utwardzania polikondensacyjnego mieszaniny cieczy jonowej z PDMS pozwoliła wyłonić najodpowiedniejsze membrany do procesu perwaporacji. Obserwowane strumienie procesowe były relatywnie niskie i wynikały z dodatkowych oporów spowodowanych grubością warstwy PDMS.

Słowa kluczowe: membrana, ciecz jonowa, perwaporacja, biobutanol

Varia

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