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Roman BABKO[1], Tatiana KUZMINA[2], Grzegorz ŁAGÓD[3]
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ANALYSIS OF THE PERIPHYTON COMMUNITIES AT THE MUNICIPAL WASTEWATER TREATMENT PLANT – CASE STUDY

ANALIZA ZBIOROWISK PERYFITONU MIEJSKIEJ OCZYSZCZALNI ŚCIEKÓW

Abstract: There was studied the composition of periphyton and its quantitative development during different stages of wastewater treatment in the flow type purification plant with the biological part working as a modified bardenpho system (Hajdow, Lublin). The periphyton samples were taken from the walls of the object at all main stages of water purification. In the composition of periphyton there were identified the following groups of organisms: algae, fungi, flagellates, testate amoeba, ciliates, rotifers and nematodes. Towards the end of purification process in periphyton of successive chambers, the part of metazoa and protozoa has increased while the abundance of flagellates has decreased. In all of the studied sampling points, the basis of periphyton community was formed by protozoa and metazoa: their part ranged from 75 to 95 %. The periphyton structure regardless of forming conditions shows similar tendencies, determined by the general conditions of a system, in which from initial stages of the purification till its end the amount of organic matters in environment decreases.

Keywords: periphyton, communities, municipal wastewater treatment plant (WWTP), protozoa, metazoa

Introduction

The periphyton is observed on all surfaces dipped into the water. It creates disturbances for technical facilities (*eg* water pipes, industrial water coolers etc.), pollutes water with biological components of fouling, but also could provide biological

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treatment of wastewater and indicates the quality of purification plant work. The biofilm was studied mostly in purification systems, where it was the main instrument and process factor of sewage treatment.

Many publications are devoted to studies of physical characteristics and physiological activity of biofilms and bacterial component of them [1–7]. At the same time relatively small amount of works provides information concerning other organisms that together with bacteria are regular components of biofilm and have certain influence on bacteria life activity and on purification process performed by the biofilm community. For example the work of Madoni [8] contains data about biofilms protozoa from rotating biological contactors (RBC) and percolating filters. The results of studies of protozoa in percolating filters have been given by some authors [9–13].

The lists of species found in RBC systems were mentioned by such authors as Madoni, Madoni and Ghetti [14, 15]. The results of research of ciliate populations and their distribution in RBC systems can be found in the following works: [15–22]. It was elicited that heterotrophic flagellates and free-swimming ciliates such as *Cyclidium glaucoma* and *Colpidium colpoda* are dominant at the early stages of wastewater purification when load of organic is higher, while shell amoebae and attached ciliates such as *Epistylis plicatilis* and *Zoothamnium procerius* dominate at the finale stage that is characterized with low BOD_5 level. There are given data concerning biomass of ciliates in biofilms of RBC [12]. Moreover, there are also evidence that besides of bacteria, the most numerous and important organisms in biofilm of RBC are ciliates [23].

Metazoa are also an important part of biofilm community, taking in consideration that they often reach big quantities and are an influential links of trophic chains [24–28].

Today, there is not enough information to specify which role does periphyton plays in treatment facilities as bioreactors with activated sludge working in flow-mode or as an SBR. About periphyton – biofilm growing unconsciously at the wall of purification facilities submerged in wastewater, it is known much less than about activated sludge that is functioning in bioreactors. Within the periphyton structure in bioreactors there are such groups of organisms to find as bacteria, fungi, algae, rhizopods, flagellates, ciliates, rotifera, nematodes [29].

At the same time there are many questions that are still awaiting answers as for example – how far is the process of biofilm and activated sludge organisms exchange (components of biocoenosis) influences the forming of activated sludge structure. How does biofilm react to negative (destructive) factors that periodically influence the water treatment system (*eg* adverse temperature, adverse pH, disturbances in aeration process, chemical toxicants etc.) and if organisms of periphyton play any important role in restoration of activated sludge biocoenosis.

The work deals with the study of main periphyton groups structure and their quantitative development at different stages of wastewater purification. The analysis of structure dynamics and diversity of main periphyton groups according to purification stage can provide additional information concerning stability of mentioned processes and likely destabilization of activated sludge structure and properties.

Materials and methods

The research material comprised periphyton sampled from the main line of technological system of the "Hajdow" mechanical-biological wastewater treatment plant in Lublin (south-eastern Poland). The studies of periphyton during main stages of sewage purification were conducted in spring when activated sludge was not in optimal conditions. In the aeration chamber the initial stages of activated sludge bulking and foaming were observed.

The samples of periphyton from the walls of main chambers were analyzed to calculate the quantities of main hydrobiont groups, such as flagellates, testate amoebae, rotifers, nematodes, ciliates, algae and fungi. Ciliates were analyzed according to their ecological groups – attached ciliates, crawling ciliates, swimming ciliates.

The samples were taken with a scraper ca. 15 cm below the sewage surface in each device. The periphyton was sampled from an area of approximately 100 cm^2.

The sampling points were: 1 – screen chamber, 2 – grit chamber, 3 – primary clarifier, 4 – anaerobic chamber, 5 – anoxic chamber, 6 – aeration chamber, 7 – secondary clarifier, 8 – recirculation chamber.

The samples were placed in containers, which were filled up to 1/3 of the volume with clarified wastewater sampled from the periphyton collection site. The samples were transferred to the laboratory for microscopic analyses and stored in a refrigerator at a temperature of 7 ^{o}C before use.

The samples were analysed under a transmitted-light with bright-field using optical microscope Opta-Tech with a magnification of 100, 250, and 400x. The method of data preparation for counting the organisms involved taking digital images of 21 non-overlapping crosswise fields of view along the major axes of symmetry of the cover slip for each of the magnifications applied. Digital archiving of each field of view allowed possible re-verification of the counting results if necessary.

Organisms analysed in the fields of view were identified and classified into the following morphological previously mentioned groups: fungi, flagellates, algae, testate amoebae, ciliates, rotifers, and nematodes. The number of the organisms within all fields of view from material sampled in one point was regarded as one replicate. Presented in article data are averaged from two months of experiment – sampling period one week.

Results and discussion

Using data concerning the number of different groups of organisms in periphyton there was analyzed the similarity of conditions at the studied sampling points applying PCA method. The sampling points are grouped as shown on Fig. 1.

Consecutive location of sampling points № 1, 2, 4, 5, 6 on the picture reflects the gradual changes in environment from the start of purification process (screen chamber) till its ending (aeration chamber). These two points are united with conditions of flowage. Either raw sewage or sewage with activated sludge flows through these chambers uninterruptedly.

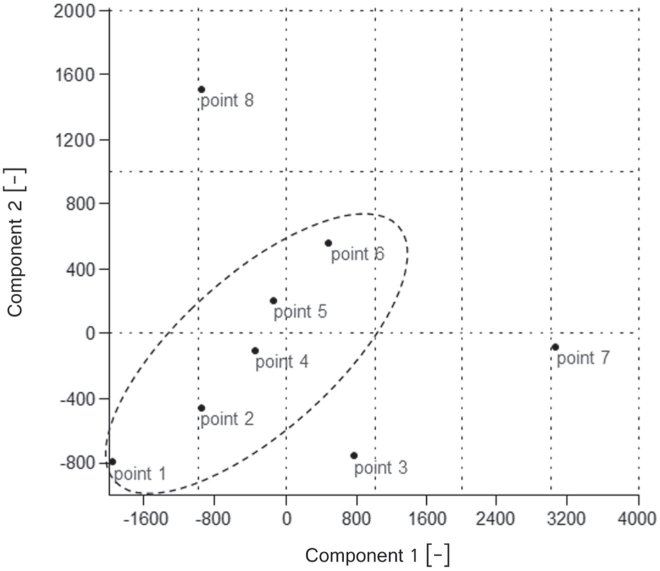

Fig. 1. PCA ordination diagram of the sampling points of the treatment plants “Hajdow”. The sampling points: 1 – screen chamber, 2 – grit chamber, 3 – primary clarifier, 4 – anaerobic chamber, 5 – anoxic chamber, 6 – aeration chamber, 7 – secondary clarifier, 8 – recirculation chamber

The specific of condition differences in primary clarifier chamber (point 3), secondary clarifier (point 7) and recirculation chamber (point 8) caused the forming of other periphyton group inside them. Points’ 3 and 7 obvious moving main group is probably caused by the fact that conditions in primary clarifier develop during the sedimentation of raw sewage that came through preliminary mechanical treatment. Meanwhile, in the secondary clarifier periphyton undergoes the influence of sewage after treatment. The conditions in recirculation chamber form, under the influence of turbulent, stream of concentrated activated sludge. In this way, the diagram confirms significant influence of chambers conditions on periphyton.

The analysis of periphyton communities in studied points enabled to reveal the whole number of differences in their structural organization. The total abundance of organisms in periphyton showed that points 3, 7 and 8 drop out of the general line (Fig. 2). The total abundance of organisms in periphyton showed that points 3, 7 and 8 drop out of the general line (Fig. 2). In fact attention can be focused on the increase in the total abundance in primary and secondary clarifiers (point 3 and point 7) and on noticeable reduction of abundance in recirculation chamber. Probably these differences are connected to conditions in the settling tanks (clarifiers) where the water flow is minimal.

Concerning decrease in the organisms’ abundance in the recirculation chamber one can assume that intensive splashing of concentrated activated sludge on the walls of the chamber may mechanically and adversely affect the periphyton. An increase in the total abundance at certain points as well as its decrease are obviously determined not by an

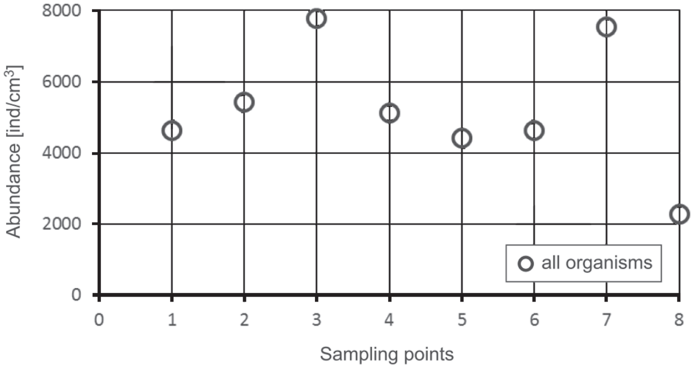

Fig. 2. Total abundance of the organisms in periphyton along the treatment plant. The sampling points: 1 – screen chamber, 2 – grit chamber, 3 – primary clarifier, 4 – anaerobic chamber, 5 – anoxic chamber, 6 – aeration chamber, 7 – secondary clarifier, 8 – recirculation chamber

even increase of each system component but by the reaction of certain groups for which the conditions become more optimal. For example nematodes do not show distinct dependence of abundance on the conditions, although there was some increase of them observed in the secondary clarifier.

At the same time rotifers have clearly increased their populations' density exactly in periphyton conditions in clarifiers (Fig. 3.).

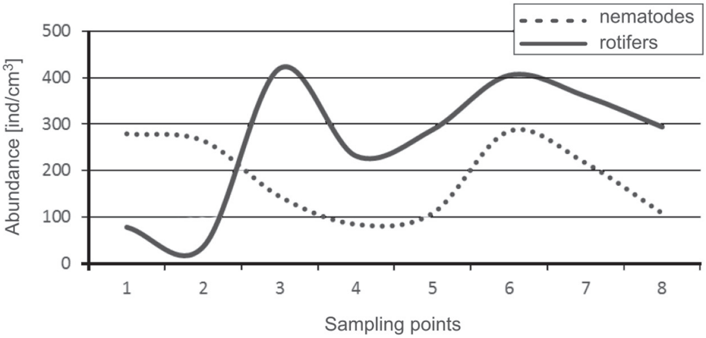

Fig. 3. Abundance of nematodes and rotifers in periphyton along the treatment plant. The sampling points: 1 – screen chamber, 2 – grit chamber, 3 – primary clarifier, 4 – anaerobic chamber, 5 – anoxic chamber, 6 – aeration chamber, 7 – secondary clarifier, 8 – recirculation chamber

Quite an independent tendency showed testate amoebae and flagellates. The average values of testate amoebae abundance were decreasing insignificantly from the beginning till the end of purification process. Meanwhile by flagellates this tendency was quite explicit (Fig. 4). Since the beginning of the process their abundance has decreased by 30 times. It is obvious that small flagellates propagate fast in the water rich in organic matters and with minimum oxygen saturation. All this matches with their high abundance during those stages of purification, where activated sludge was not involved.

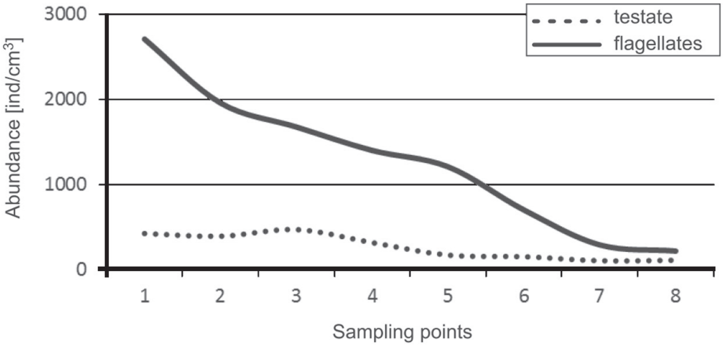

Fig. 4. Abundance of testate amoeba and flagellates in periphyton along the treatment plant. The sampling points: 1 – screen chamber, 2 – grit chamber, 3 – primary clarifier, 4 – anaerobic chamber, 5 – anoxic chamber, 6 – aeration chamber, 7 – secondary clarifier, 8 – recirculation chamber

Ciliates reached the maximum abundance in the clarifiers Fig. 5.

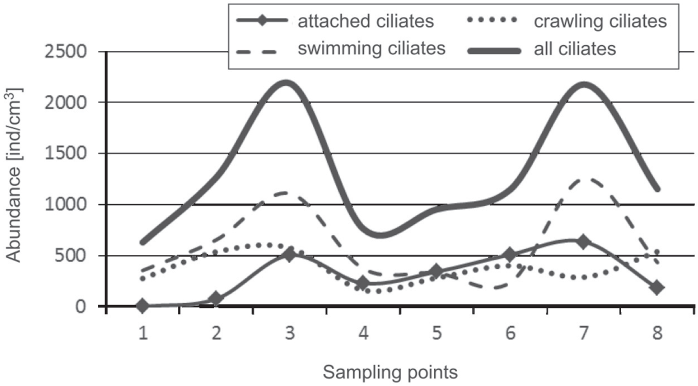

Fig. 5. Abundance of ciliates in periphyton along the treatment plant. The sampling points: 1 – screen chamber, 2 – grit chamber, 3 – primary clarifier, 4 – anaerobic chamber, 5 – anoxic chamber, 6 – aeration chamber, 7 – secondary clarifier, 8 – recirculation chamber

At the same time the general tendency was caused mainly by specimen of free-swimming ciliates. The specimen of attached ciliates and crawling ciliates did not show pronounced increase in abundance in conditions of clarifiers. At the same time attached ciliates specimen were only minimally present at the initial stages of purification and significantly reduced their abundance in the conditions of recirculation chamber. Such a relation between various forms of ciliated protozoa can be partially explained by the fact that attached ciliates present in the periphyton must propagate within it too, while free-swimming ciliates as well as crawling ciliates can penetrate the periphyton from the outside and rapidly increase their abundance. This can be considered from the perspective of ability of ciliates from different ecologic groups to act as bioindicators. Treatment facilities such as aerotanks usually operate on the basis of heterotrophic communities and their autotrophic component is minimized. Therefore, the question of establishing a potential part of autotrophes in periphyton of treatment plants is of a big interest.

The nature of the quantitative representation of algae and fungi recorded at various points during this study is presented in Fig. 6.

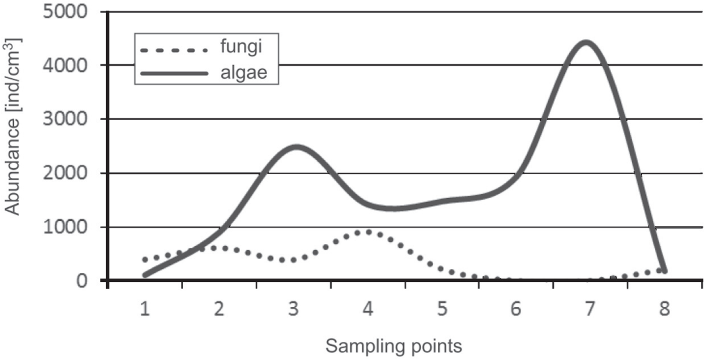

Fig. 6. Abundance of algae and fungi in periphyton along the treatment plant. The sampling points: 1 – screen chamber, 2 – grit chamber, 3 – primary clarifier, 4 – anaerobic chamber, 5 – anoxic chamber, 6 – aeration chamber, 7 – secondary clarifier, 8 – recirculation chamber

The figure shows that ecological optimum in the conditions of clarifiers had algae; their abundance grew a lot in primary clarifier where water transparency was the highest among all studied points. As to fungi, the decrease of their number during purification indicates that optimum for these organisms are eutrophic and anoxic conditions. The role of heterotrophic and autotrophic organisms in the periphyton structure in the conditions of treatment plant is shown in Fig. 7.

According to proportion in all the chambers the basis of the periphyton community was formed with protozoa and metazoa. Their part at various purification stages was from 75 % to 95 %.Together with fungi the part of heterotrophic organisms in periphyton can reach 99 %. The part of fungi in various stages of purification was not higher than 8 %, while autotrophic organisms formed from 1 % to 25 % of all organisms' abundance. Since PCA analysis was performed based on the relative number of organism groups in the gradient of conditions that are determined by a continuous process of purification, it can be concluded that consolidation of most organisms groups (lower right quarter of the diagram) is caused by their connection with dynamics of the processes (Fig. 8).

At the same time considerable remoteness of flagellates and algae from the main group indicates resultant influence of external factors on them. It is clear that algae directly depend on illumination intensity and flagellates – on the level of organic matters. Thus, the flagellate dynamics will be rather determined by disturbances of the purification process or excessive inflow of wastewater. According to Curds [30] flagellates predominate in the system in the early stages only because of their lower energy requirements. Heterotrophic flagellates are therefore recognized as indicators of

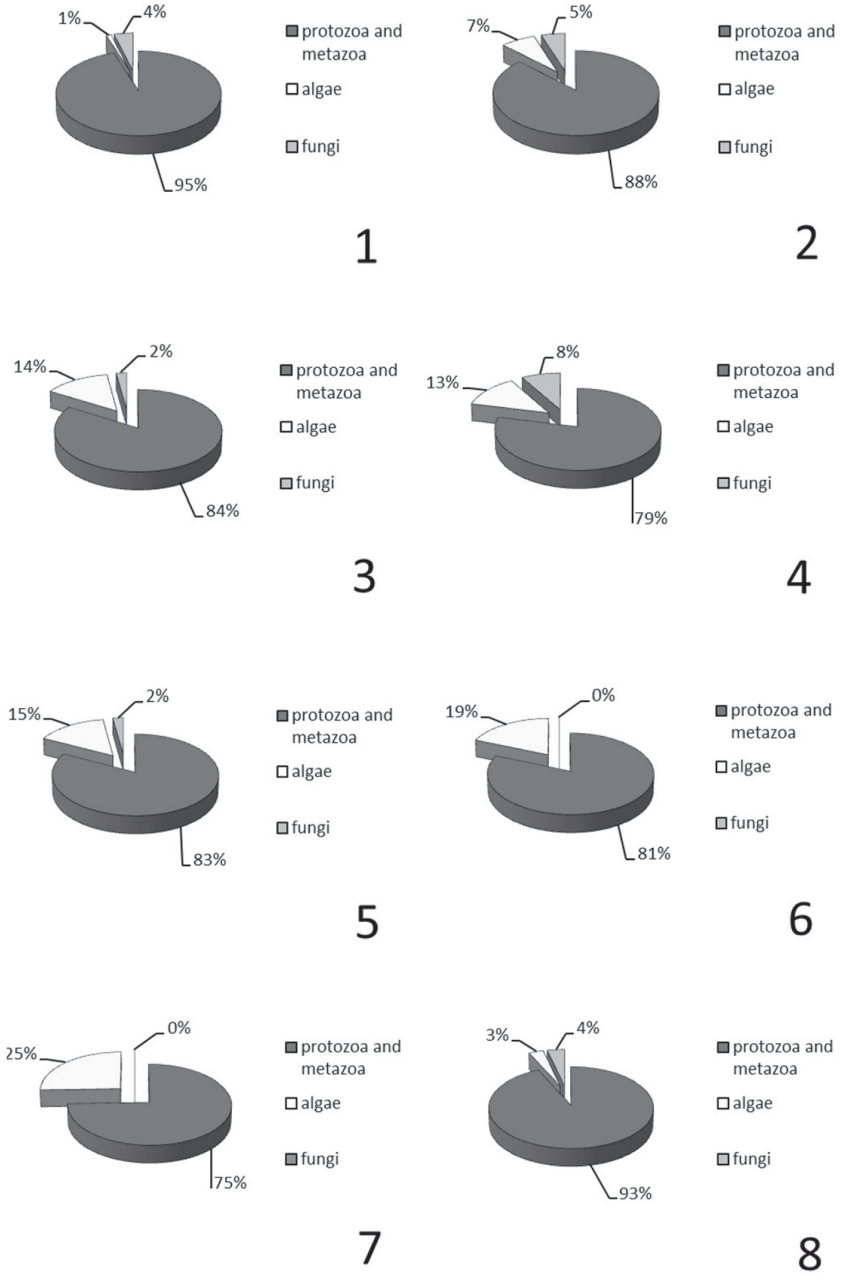

Fig. 7. The ratio of the quantitative representation of different groups of organisms in the structure of periphyton community along the treatment plant. The sampling points: 1 – screen chamber, 2 – grit chamber, 3 – primary clarifier, 4 – anaerobic chamber, 5 – anoxic chamber, 6 – aeration chamber, 7 – secondary clarifier, 8 – recirculation chamber

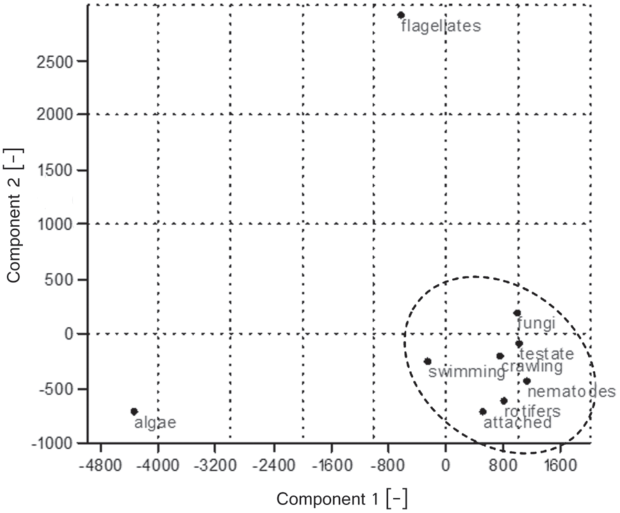

Fig. 8. PCA ordination diagram of the different groups of organisms in the structure periphyton community in the conditions of treatment plant

malfunction of treatment facilities or their overload [8, 12]. There is direct relation between dynamics of algae, fluctuations in illumination intensity and efficiency of water clarification process. During the study period there was a tendency observed – towards the end of purification process the part of metazoa and protozoa in periphyton of successive chambers was increasing (Fig 9). Similar results were obtained at RBC type water treatment plant [23].

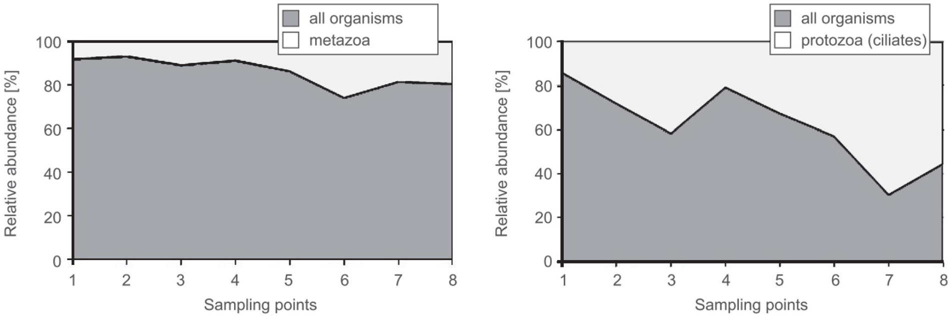

Fig. 9. Part of metazoan (A) and ciliates (B) in the total abundance of organisms in periphyton along the treatment plant. The sampling points: 1 – screen chamber, 2 – grit chamber, 3 – primary clarifier, 4 – anaerobic chamber, 5 – anoxic chamber, 6 – aeration chamber, 7 – secondary clarifier, 8 – recirculation chamber

In periphyton (RBC) the most numerous group of organisms was ciliates (55–95 % of the total quantity). In the periphyton conditions of flow type purification plant in the modified system bardenpho, equal to plant Hajdow protozoa make up from 14 % to 69 %.Similarly behaved the small flagellate – in treatment plant Hajdow as well as in (RBC) their number was reducing by the end of purification process (Fig. 4). Thus, the structure of periphyton irrespective of its forming conditions shows similar tendencies, determined by the general conditions of system in which from the initial stages and till the end, the amount of organic matters in environment decreases.

Summary and conclusions

The periphyton community in successive chambers of flow type treatment plant with the biological part functioning in the modified system bardenpho, reached maximum abundance in primary and secondary clarifiers. Concerning clarifiers, the maximum abundance was reached by algae, rotifers and ciliates. The abundance of flagellates from the start to the end of the purification process decreased of more than 30 times. Towards the end of purification process of periphyton in successive chambers, the amount of protozoa and metazoa has increased. In all of the studied sampling points, the basis of periphyton community was formed by protozoa and metazoan, their part made up 75–95 %. The part of heterotrophs reached 99 % and part of autotrophes varied from 1 % to 25 %

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Abstrakt: W pracy zaprezentowano badania składu peryfitonu i jego rozwój ilościowy podczas kolejnych etapów oczyszczania ścieków w miejskiej oczyszczalni ścieków Hajdów w Lublinie, której część biologiczna pracuje w technologii zmodyfikowanego systemu bardenpho. Próby peryfitonu pobierano z powierzchni ścian obiektów na wszystkich głównych etapach oczyszczania ścieków. W składzie peryfitonu zostały zidentyfikowane następujące grupy organizmów: glony, grzyby, wiciowce, ameby skorupkowe, orzęski, wrotki i nicienie. W kolejnych analizowanych urządzeniach zlokalizowanych w ciągu technologicznym oczyszczalni peryfiton wykazywał wzrost ilości organizmów w obrębie grup metazoa i pierwotniaków, podczas gdy liczebność wiciowców uległa zmniejszeniu. We wszystkich badanych punktach pomiarowych podstawa zbiorowisk peryfitonu utworzona była przez pierwotniaki i metazoa, ich udział wahał się od 75 do 95 %. Struktura peryfitonu badanych urządzeń wykazuje podobne tendencje, uzależnione od warunków panujących w poszczególnych urządzeniach, w którym od pierwszych etapów oczyszczania aż do jego końca ilość dostępnych substancji organicznych maleje.

Słowa kluczowe: peryfiton, zbiorowiska, komunalna oczyszczalnia ścieków, pierwotniaki, metazoa

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KINETIC ANALYSIS OF CO FORMATION UNDER OXY-COMBUSTION CONDITIONS

KINETYCZNA ANALIZA POWSTAWANIA CO W WARUNKACH OKSY-SPALANIA

Abstract: The paper reports the results of numerical computations concerning the formation of CO in the kinetic flame during natural gas oxy-combustion. The effect of temperature, reagent residence time and the composition of an atmosphere containing CO_2 with 21 and 29 vol % O_2 on the variation of CO concentration in the flame was examined. The oxy-combustion process was conducted with a 25 % excess oxygen. The analysis of reactions in flames at temperatures of 1500 K and 1800 K was performed within the Chemked II program using the combustion mechanism proposed by Mendiara & Glarborg, which includes 779 reactions. The computation results have confirmed that the rate of the key reactions responsible for the production of CO in the flame depends on the flame temperature and the oxy-combustion temperature. The peak CO concentrations are higher for the oxidizing mixture containing 29 vol % O_2. After attaining a maximum, the CO flame concentration drops faster for an atmosphere richer in oxygen. The longer the time of reagent residence in the flame region, the lower the CO concentration. In different atmospheres and at different combustion temperatures, an identical CO level can be achieved in wet combustion gas. Irrespective of the temperature and atmosphere of oxy-combustion, most CO is produced as a result of the reaction $OH + CO \rightleftharpoons HCO_2$. The reduction of oxygen in the oxidizing atmosphere at flame temperatures of 1500 and 1800 K lowers the CO production in the dominant reactions responsible for CO formation. The contribution of individual reactions in the CO production for the identical atmospheres is different with varying temperature. In the case of the reaction $HCO + O_2 \rightleftharpoons HO_2 + CO$, the temperature increase reduces the CO production. A reverse dependence of CO production on temperature characterizes the reaction $H_2 + CO + M \rightleftharpoons CH_2O + M$. In addition, change in temperature changes the order in which the dominant reactions occur. Within the residence time equal to 100 ms, two periods of intensified CO production and consumption can be identified. The peak concentrations of H, OH and O radicals in the flame attain a maximum within the same time; as time goes by, the highest concentration is achieved by OH radicals. The presence of considerable levels of CO_2 in the combustion substrates has an inhibiting effect on the natural gas oxidation process.

Keywords: oxy-combustion, flame CO concentration, combustion kinetics

Introduction

In the face of increasing concerns about climatic changes resulting from greenhouse gas emissions, CO_2 capture and storage technologies are the subject of intensive studies

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in Poland [1–3]. One of the techniques facilitating CO_2 capture is oxy-combustion. The source of oxygen may be a carrier, *eg* NiO during fluidized-bed combustion [4] or air. In view of the too high temperature of combustion in oxygen, its dilution with CO_2 is used. The combustion gas from oxy-combustion consists mainly of carbon dioxide and water vapour, and the capture of CO_2 is done by condensing the water vapour. The combustion gas carbon dioxide can be partially recycled and reintroduced to the combustion chamber as a cooling medium. Studies on the addition of CO_2 to methane are focused on the supply of gas turbines with the CH_4-CO_2 mixture. The CH_4-CO_2 mixture may originate from the anaerobic fermentation of biomass or organic industrial wastes [5].

The total elimination of nitrogen from the oxy-combustion process is impossible due to the insufficient oxygen purity, combustion chamber leakage or the nitrogen content of fuel. Nevertheless, oxy-combustion allows the NO_x concentration to be reduced as low as to 50 % compared to air combustion [6].

Substituting N_2 with CO_2 in the combustion mix (as compared to air) has an effect on, *eg*,: adiabatic flame temperature, combustion rate, flame stability, the transfer and thermal properties of combustion gas, the rate of chemical reactions and heat radiation.

As the specific heat of CO_2 is higher than that of N_2, more energy is needed for raising the temperature of the mixture. Therefore, for the same oxygen fraction of the oxidizer and excess air, the adiabatic flame temperature in the CO_2/O_2 mixture is lower than in N_2/O_2 [7]. To achieve the identical temperature as for air, a higher percentage oxygen fraction of the oxidizer will be needed for oxygen combustion.

For each oxygen-fuel flame, an operation zone can be determined. Four critical problems are distinguished, which may light limit the flame operation zone; these are: flameout, burner flashback, combustion instability and spontaneous ignition. Also pressure fluctuations caused by heat release in the combustion chamber may contribute to instability in oxy-combustion [8].

Glarborg and Bentzen [9] interpreted experimental results using a detailed mechanism of hydrocarbon oxidation. They have concluded that the high CO_2 concentration around the burner prevents the complete oxidation of fuel at temperatures higher than 1200 K, in spite of the presence of oxygen. The increased CO concentration in oxy-combustion flue gas is explained by the reactions of CO_2 with free radical and the dissociation of CO_2 [9–15]. Carbon monoxide forms, inter alia, as a result of the reaction of CO_2 with:

a) hydrogen radicals:

$$OH + CO \rightleftharpoons H + CO_2 \tag{1}$$

which competes with the reaction:

$$H + O_2 \rightleftharpoons O + OH \tag{2}$$

for H radicals. Reaction (1) proceeds relatively fast, even at lower temperatures. In that case, the concentration of H and O radicals in the flame is reduced, which is associated with a drop in the fuel combustion rate [12].

b) oxygen radicals:

$$CO_2 + O \rightleftharpoons CO + O_2 \tag{3}$$

c) hydroxide radicals:

$$CO_2 + OH \rightleftarrows CO + HO_2 \tag{4}$$

The reactions of CO_2 with O and OH radicals are too slow to be able to play a significant role.

d) hydrocarbon radicals:

$$CH_3 + CO_2 \rightleftarrows CH_3O + CO \tag{5}$$

$$CH_2 + CO_2 \rightleftarrows CH_2O + CO \tag{6}$$

$$CH + CO_2 \rightleftarrows HCO + CO \tag{7}$$

These reactions have no significant importance due to the low contents of these radicals of natural gas flame. Hydrocarbon radicals containing one carbon atom are less reactive that those containing two carbon atoms, such as HCCO.

The double bonds existing between the carbon and oxygen atoms in CO_2 make the thermal dissociation of CO_2 difficult. At high temperatures, the reaction of thermal dissociation of CO_2 (which is strongly endothermic) may occur in the presence of a high-energy body, M:

$$CO_2 + M \rightleftarrows CO + O + M \tag{8}$$

The above-mentioned reaction occur in the flame and in the after-flame zone, depending on the burner and combustion chamber designs. The examination of the peak concentrations of reagents in the flame in the combustion process are of key importance. Experiments and numerical computations carried out using three different combustion mechanisms have shown that the peak CO concentrations in the flame during methane combustion in air increase with increasing CO_2 addition to the air-fuel mixture [10].

The effect of oxy-combustion stoichiometry and the reagent residence time are also reflected in the combustion gas CO level [14]. With the reduction of the reagent combustion chamber residence time, a rise in CO concentration and an increase in temperature occur.

Combustion kinetics

The description of reactions occurring in the flame is extremely difficult and depends on numerous factors, such as temperature, pressure, burner type, fuel and oxidizing mixture compositions, etc. Depending the number of reagents and their stoichiometric coefficients, first-, second- and third-order reactions are distinguished.

For the general notation of the reaction:

$$\sum_{i=1}^{n} \nu'_{ij} Z_i \underset{k_r}{\overset{k_f}{\rightleftarrows}} \sum_{i=1}^{n} \nu''_{ij} Z_i \tag{9}$$

whose order can be expressed as follows:

$$m = \sum_{i=1}^{n} v'_{ij} \tag{10}$$

the reaction rate constant for an any-order reaction running to the right, k_f, or to the left, k_r , is determined using the modified Arrhenius equation:

$$k = AT^{\beta}\, e^{-\frac{E_a}{RT}} \tag{11}$$

The resultant rate of production of the component Z_i is the sum for the reaction "j" running to the left-hand and the right-hand direction, respectively:

$$\left(\frac{d\{Z_i\}}{dt}\right)_j = (\nu''_{ij} - \nu'_{ij})[k_f \Pi_i \{Z_i\}^{\nu'_{ij}} - k_r \Pi_i \{Z_i\}^{\nu''_{ij}}] \tag{12}$$

The total rate of production of the component Z_i is determined by summing all reactions:

$$\frac{d\{Z_i\}}{dt} = \sum_{j=1}^{N}\left(\frac{d\{Z_i\}}{dt}\right)_j \tag{13}$$

The concentration is denoted with the brace { }. In the presented calculation results, the concentration is expressed in moles per unit of reaction product mass in the reactor under examination [16].

The mechanism of combustion of hydrocarbons consists of many consecutive, as well as overlapping, elementary reactions of different rates. The reactions describe combustion stages, such as the attack on the fuel molecule, the formation of a "bank" of radicals, the recombinations of radicals, oxidation, etc. Several dozen detailed models dedicated to the combustion of solid, liquid and gaseous fuels function in the literature on the subject. Detailed combustion mechanisms have been developed based on the following experimentally determined values: the coefficients of the gaseous phase reaction rate constant, laminar combustion rates, laminar flame concentration variation profiles, and ignition delay times. The most common natural gas combustion mechanisms include: GRI-Mech [17] and those developed by Konnov [18] and Mendiara, Glarborg [19]. The above-mentioned reaction mechanisms differ in the number of reactions, chemical compounds and elements and the values of activation energy E_a and the constants A, β.

Computation data and procedure

Modelling of the natural gas combustion kinetics was performed in the present study within the Chemked II software program, version 3.5.2 [20], using the combustion mechanism proposed by Mendiara, Glarborg [19] and an extended thermodynamic database [17]. The combustion mechanism includes 779 elementary reactions between 97 chemical compounds. The ideal mixing of the combustion substrates in the burner was assumed for the computation. The solver of the program Chemked II uses the thermodynamic database [17].

The computation was conducted for flame temperatures of 1500 K and 1800 K with a constant pressure of p = 0.1 MPa. The reagent flame residence was 100 ms. The examined temperature values were achieved by averaging the results of temperature measurements done in the flame of a low-swirl kinetic burner installed in the combustion chamber. The results of the above-mentioned tests have not been published yet. The natural gas composition was as follows: CH_4 = 98 %; C_2H_6 = 0.6 %; C_3H_8 = 0.3 %; N_2 = 1 %; CO_2 = 0.1 %. Oxy-combustion with a 25 % excess oxygen was conducted. The following oxy-combustion atmospheres were examined: 21 % O_2/79 % CO_2 and 29 % O_2/71 % CO_2. Constant values of natural gas and oxygen were examined. The computation was started from the mixture 29 % O_2/71 % CO_2 and then CO_2 was added, thus causing, at the same time, a decrease in the oxygen fraction and an increase in mixture mass.

Computation results

The presented concentrations of free radicals and carbon monoxide relate to wet combustion gas and are expressed in moles of the substance per 1 gram of the reaction product. Figure 1 represents the profiles of CO flame concentration variations as a function of temperature and oxidizing mixture composition. As follows from the

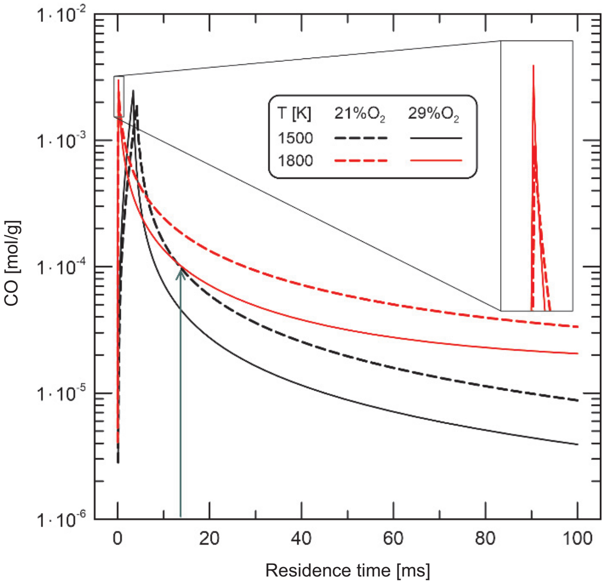

Fig. 1. CO flame concentration as a function of residence time

figure, the peak CO concentrations are higher for the oxidizing mixture containing 29 vol. % O_2. After attaining the maximum, the CO flame concentration drops faster for the atmosphere richer in oxygen. The longer the time of reagent residence in the flame region, the lower the CO concentration. In different atmospheres and at different combustion temperatures, an identical CO content of wet combustion gas can be obtained, as displayed in the diagram for a residence time of approx. 13 ms.

For each of the considered oxy-combustion variants, the key reactions responsible for CO production in the kinetic flame are detailed in Figs. 2a–d. The term CO production

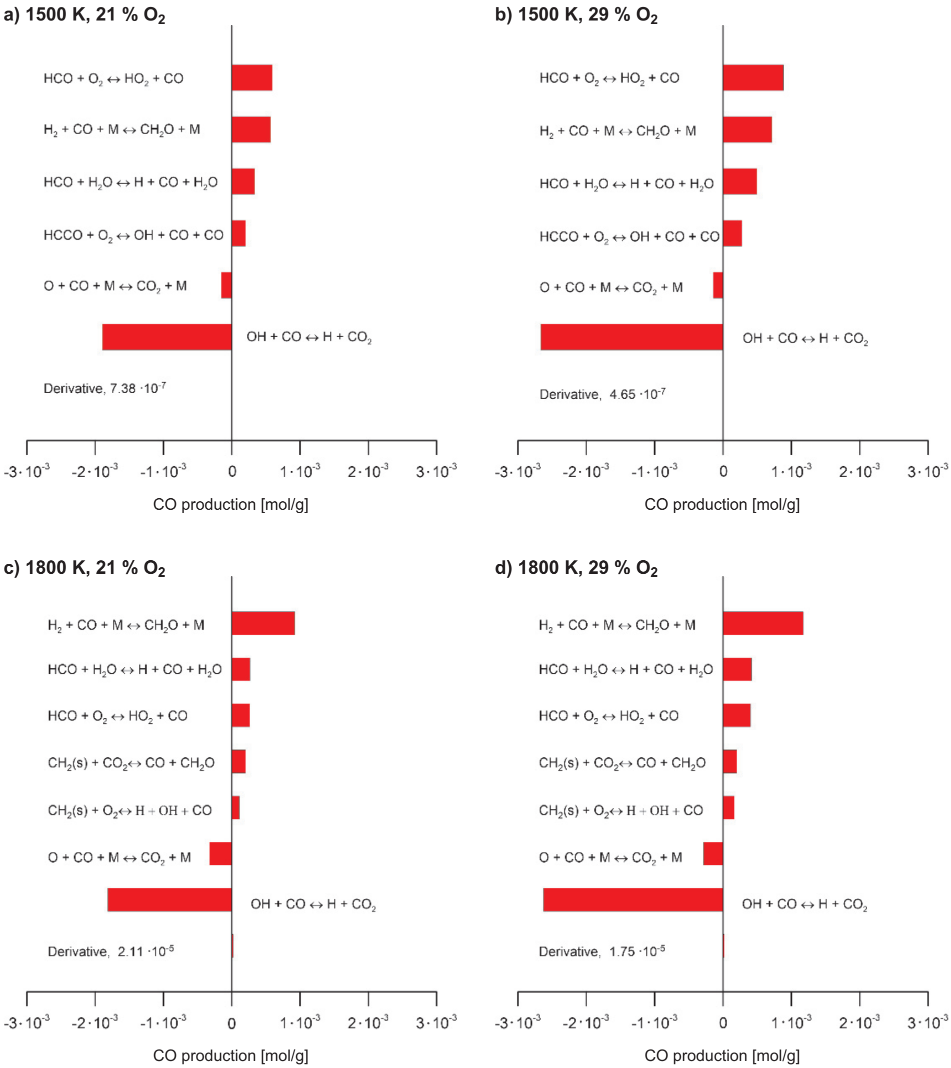

Fig. 2. The key reactions of CO formation for λ = 1.25 as a function of temperature and atmosphere composition: a) 1500 21 % O_2; b) 1500 29 % O_2; c) 1800 21 % O_2; d) 1800 29 % O_2

should be understood as the number of CO moles contained in 1 gram of products within a residence time of 100 ms.

Irrespective of temperature and combustion atmosphere, most CO is produced as a result of the reaction $OH + CO \rightleftharpoons H + CO_2$. The reduction of oxygen in the oxidizing atmosphere at flame temperatures of 1500 and 1800 K lowers the CO production in the predominant reactions responsible for CO formation. The contribution of individual reactions in the CO production for the identical atmospheres is different with varying temperature. For the reaction $HCO + O_2 \rightleftharpoons HO_2 + CO$, the increase in temperature reduces the CO production and lowers the position held (from 2 to 4). A reverse dependence of CO production on temperature characterizes the reaction $H_2 + CO + M \rightleftharpoons CH_2O + M$. In addition, changing the temperature from 1500 K to 1800 K results in a new reaction, $CH_{2(s)} + O_2 \rightleftharpoons H + OH + CO$, to arise in the fifth position in place of the reaction $HCCO + O_2 \rightleftharpoons OH + CO + CO$.

The overall CO production/consumption rate, in accordance with Eq. (13) for the considered oxy-combustion variants, is illustrated in Fig. 3. Within the examined residence time, two periods of intensified CO production and consumption can be identified. Figure 3 highlights the differences in the overall reaction rate associated with the change in the temperature and O_2/CO_2 atmosphere.

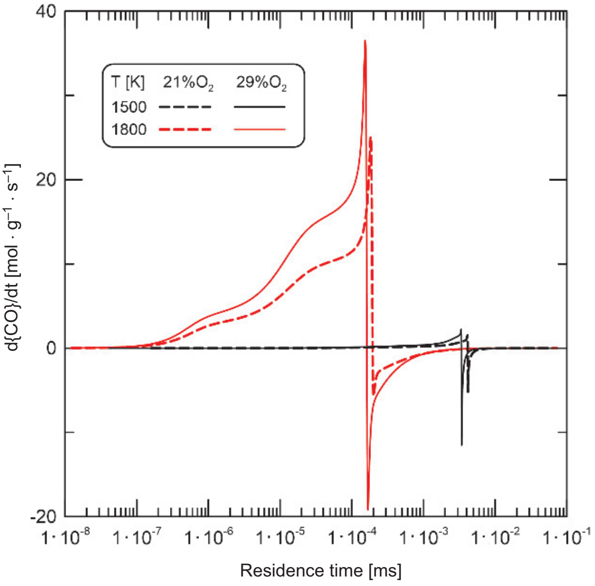

Fig. 3. Variations in CO production rate in time

The selected reactions may occur due to the formation of a free radical "bank". According to the reaction (1) proceeding in the left-hand direction, the H radicals are used, while OH radicals form. The peak concentrations of H, OH and O radicals attain a maximum within a time identical to that shown in Fig. 4. After a duration of 12 ms, there are most OH radicals in the flame.

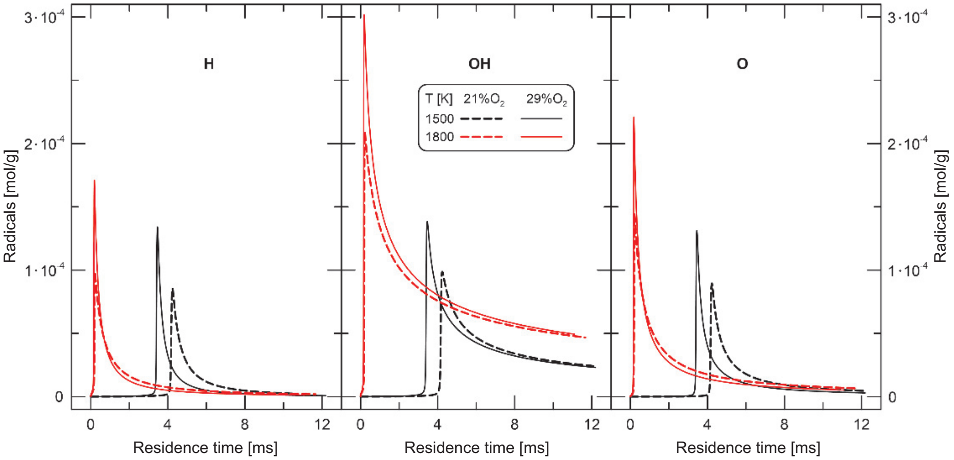

Fig. 4. The peak concentrations of H, OH and O in the flame

Conclusions

The interpretation of the computation results for natural gas oxy-combustion in atmospheres containing CO_2 and 21 % O_2 and 29 % O_2 has enabled the following conclusions to be drawn:

1. The peak CO concentrations are higher for the oxidizing mixture containing 29 vol % O_2. After attaining the maximum, the CO flame concentration drops faster for the atmosphere richer in oxygen.

2. The longer the time of reagent residence in the flame region, the lower the CO concentration.

3. Many reactions are responsible for the formation of CO in the flame, with the primary being $OH + CO \rightleftarrows H + CO_2$. A reaction classified as second in terms of CO formation rate is $HCCO + O_2 \rightleftarrows OH + CO + CO$.

4. Irrespective of temperature and combustion atmosphere, most CO is produced as a result of the reaction $OH + CO \rightleftarrows H + CO_2$.

5. The reduction of oxygen in the oxidizing atmosphere at flame temperatures of 1500 and 1800 K lowers the CO production in the predominant reactions responsible for CO formation.

6. The contribution of individual reactions in the CO production for the identical atmospheres is different with varying temperature. For the reaction $HCO + O_2 \rightleftarrows HO_2 + CO$, the increase in temperature reduces the CO production and lowers the position held.

7. Carbon monoxide forms very fast in the flame in the oxy-combustion process, as indicated by its maximum concentrations in the vicinity of the burner. However, the oxidation of carbon monoxide to CO_2 is much slower, which is due to the decrease in the CO molar fractions with increasing residence time.

8. The peak concentrations of H, OH and O radicals attain a maximum within the same.

Nomenclature

A – pre-exponential factor $[(\mathrm{cm}^3 \cdot \mathrm{mol}^{-1})^{m-1} \cdot \mathrm{s}^{-1}]$
E_a – activation energy of a chemical reaction $[\mathrm{J} \cdot \mathrm{mol}^{-1}]$
j – number of reactions,
k – reaction rate coefficient $[(\mathrm{cm}^3 \cdot \mathrm{mol}^{-1})^{m-1} \cdot \mathrm{s}^{-1}]$
m_i – order of a reaction [-]
M – third body [-]
R – ideal gas constant $[\mathrm{J} \cdot \mathrm{mol}^{-1} \cdot \mathrm{K}^{-1}]$
T – temperature [K]
Z_i – chemical symbol “i”
β – temperature exponent of the pre-exponential factor [-]
λ – excess of oxygen [-]
ν'_i – the stoichiometric ratio of the substrate “i” in the reaction “j” [-]
ν''_i – the stoichiometric ratio of the product “i” in the reaction “j” [-]

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KINETYCZNA ANALIZA POWSTAWANIA CO W WARUNKACH OKSY-SPALANIA

Akademia Górniczo-Hutnicza w Krakowie

Abstrakt: W pracy zaprezentowano wyniki obliczeń numerycznych dotyczących tworzenia CO w kinetycznym płomieniu podczas oksy-spalania gazu ziemnego. Badano wpływ temperatury, czasu przebywania reagentów oraz składu atmosfery zawierającej CO_2 i 21 oraz 29 % obj. O_2 na zmianę stężenia CO w płomieniu. Proces oksy-spalania prowadzony był z 25 % nadmiarem tlenu. Analizę reakcji w płomieniach o temperaturach 1500 i 1800 K przeprowadzono w programie Chemked II, z zastosowaniem mechanizmu spalania zaproponowanego przez Mendiara, Glarborg zawierającego 779 reakcji. Wyniki obliczeń potwierdziły, że szybkość najistotniejszych reakcji odpowiedzialnych za tworzenie CO w płomieniu zależy od temperatury płomienia oraz atmosfery oksy-spalania. Szczytowe stężenia CO są większe dla mieszanki utleniającej zawierającej 29 % obj. O_2. Po osiągnieciu maksimum, stężenie CO w płomieniu spada szybciej dla atmosfery bogatszej w tlen. Im dłuższy czas przebywania reagentów w obszarze płomienia, tym niższe stężenie CO. W różnych atmosferach oraz temperaturach spalania można uzyskać identyczny poziom CO w spalaniach mokrych. Bez względu na temperaturę oraz atmosferę oksy-spalania każdorazowo najwięcej CO utworzone zostaje w wyniku reakcji $OH + CO \rightleftharpoons H + CO_2$. Redukcja tlenu w atmosferze utleniającej przy temperaturach płomienia wynoszących 1500 i 1800K obniża produkcję CO w dominujących reakcjach odpowiedzialnych za tworzenie CO. Wkład poszczególnych reakcji w produkcję CO dla tych samych atmosfer ze zmianą temperatury płomienia jest zróżnicowany. W przypadku reakcji $HCO + O_2 \rightleftharpoons HO_2$ CO wzrost temperatury zmniejsza produkcję CO. Odwrotna zależność produkcji CO od temperatury charakteryzuje reakcję $H_2 + CO + M \rightleftharpoons CH_2O + M$. Dodatkowo zmiana temperatury zmienia kolejność dominujących reakcji. W zakresie czasu rezydencji równego 100 ms wyróżnić można okresy wzmożonego tworzenia oraz zużywania CO. Szczytowe stężenia rodników H, OH i O w płomieniu osiągają maksimum w tym samym czasie, a w miarę jego upływu najwyższe stężenie posiadają rodniki OH. Obecność znacznych ilości CO_2 w substratach spalania ma działanie hamujące proces utleniania gazu ziemnego.

Słowa kluczowe: oksy-spalanie, stężenie CO w płomieniu, kinetyka reakcji

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FACTORS DETERMINING THE OPTICAL PROPERTIES OF UNDERGROUND WATER INTENDED FOR HUMAN CONSUMPTION

CZYNNIKI WARUNKUJĄCE WŁAŚCIWOŚCI OPTYCZNE WÓD PODZIEMNYCH PRZEZNACZONYCH DO SPOŻYCIA

Abstract: The optical properties of water (color and turbidity) and the content of iron and manganese compounds were determined in a multi-year study of underground water in 1990–2004. Water samples were collected from 12 intake monitoring sites in the following regions: Lower Vistula Valley, Zulawy Wislane – Vistula Delta Plain, Starogard Lakeland and Ilawa Lakeland. The maximum allowable turbidity levels (1 NTU) were exceeded in raw water samples, which required treatment. The optical parameters of water were affected by iron and manganese concentrations. Water samples with, a high iron content were collected from all investigated regions. The highest iron content of raw water samples was noted in Sztum (2.50 to 6.90 mg $\cdot$ dm^{-3} total Fe), and the lowest – in Malbork (0.05 to 0.20 mg $\cdot$ dm^{-3} total Fe). The highest manganese concentrations (0.72 to 1.72 mg $\cdot$ dm^{-3}) were reported in raw water samples collected in the Zulawy Water Mains. Manganese levels ranged from 0.19 to 0.40 mg $\cdot$ dm^{-3} Mn in Sztum, and from 0.14 to 0.30 mg $\cdot$ dm^{-3} Mn in Kwidzyn. The lowest manganese concentrations were reported in raw water samples from Tertiary and Cretaceous water-bearing horizons. These samples did not require treatment.

In most cases, the flow of water through the distribution network modified the parameters of treated water. This is an adverse phenomenon, as the final product supplied to end-users may not comply with standard requirements. For this reason, optical parameters and the manganese and iron content of potable water have to be monitored regularly between the point of water intake and the end-user.

Keywords: color, turbidity, iron, manganese, water-bearing horizons, water quality

Introduction

Underground water intended for human consumption is subject to special protection, and the physical and chemical composition of water has to be monitored regularly to

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ensure that the consumers are supplied with safe potable water. In some cases, special measures have to be initiated instantly to protect both the source and the quality of water [1, 2]. According to the WHO in 1998, water is safe for human health if it meets basic sanitation requirements. Water, the indispensable element of life, has to be supplied in a satisfactory quantity and quality [3, 4]. When evaluating the quality of water, consumers rely on its organoleptic properties, in particular the optical qualities of water. Water characterized by high turbidity and an intense color which is attributed mostly to high concentrations of iron and manganese compounds, is regarded as unsafe for consumption. Water color may also be affected by the presence of colored organic substances found in the humus fraction of soil. Those substances are a potential source of energy and carbon for the microorganisms dwelling in potable water. The presence of such substances in the distribution network increases the risk of pipeline corrosion [5–7]. Yet most importantly, organic compounds found in the water mains may pose a direct health hazard [3]. Water marked by high turbidity may protect microorganisms from disinfecting agents, and it may stimulate the growth of bacteria. Iron is a natural and a commonly occurring component of underground water, and it is found in various combinations and forms. The above is caused by the continuous dissolution of minerals and the presence of carbon dioxide in water. In general, underground water is deprived of oxygen, which is why iron is found mostly in the oxidation state of +2 (Fe^{+2}) in the form of iron bicarbonate and iron sulfate. In the presence of oxygen, the above compounds are hydrolyzed, producing iron hydroxide. Iron deteriorates the taste properties of water excessive iron levels may have an adverse effect on various technological processes and may stimulate the growth of iron-oxidizing and manganese--oxidizing bacteria [5, 7, 8].

Manganese is an essential trace element, which is needed for the proper functioning of living organisms [8], yet it may also exert a toxic effect. Excess manganese causes damage to parenchymatous organs and disrupts iron metabolism [8, 9]. In underground water, manganese occurs mostly with iron in the form of bicarbonate and sulfate. Manganese is an element with multiple oxygen states which affects the water treatment process. In water, manganese is oxidized by chloride. When oxidized to Mn^{+4}, it forms insoluble manganese dioxide (MnO_2) which causes brown spots in laundry items and industrial products. Excess manganese levels deteriorate the organoleptic properties of water and, similarly to iron, they may have an adverse effect on selected technological processes. The presence of manganese in potable water may lead to sediment formation in the water distribution network [10, 11].

This paper presents the results of a multi-year study investigating the factors responsible for changes in water turbidity and color, and in the concentrations of iron and manganese between the point of water intake and the end-user.

Materials and methods

The optical properties of water (color and turbidity), iron and manganese concentrations were analyzed in 1990–2004 in samples of underground water from 12 intake monitoring sites in four Polish mesoregions: Lower Vistula Valley, Zulawy

Wislane – Vistula Delta Plain, Starogard Lakeland and Ilawa Lakeland (Table 1). The quality of water in the studied regions was evaluated in view of the water source (water intake), the applied treatment method (treatment plant), the water distribution network (end-user) and the depth of the water-bearing horizon. The studied monitoring sites were diversified with regard to their geological structure and the number and depth of wells.

Table 1

Characteristic features of potable water intakes investigated in the study

Mesoregion	Intake	Population supplied in 2004	Water-bearing horizons	Number of wells/ Well depth [well/m]	Piping material	Treatment process
Lower Vistula Valley	Male Walichnowy	833	Cretaceous	1/129 1/101.5	cast iron, steel, PVC	aeration
	Wielkie Walichnowy	850	Cretaceous	1/110	cast iron, asbestos-cement	aeration
	Gniew	7 100	Cretaceous Tertiary	1/130 1/120	cast iron, asbestos-cement	aeration, deferrisation
	Gardeja	2 864	Quaternary	1/57 1/60	cast iron, asbestos-cement	aeration, deferrisation
	Kwidzyn Kamionka	25 080	Cretaceous Tertiary	1/231 3/180,161, 163	cast iron, asbestos-cement	aeration, deferrisation
Vistula Zulawy	Zulawy Water Mains	60 000	Cretaceous Tertiary	26/35-80 1/250	cast iron, PVC, asbestos-cement	aeration, deferrisation
	Malbork	40 000	Cretaceous Tertiary	5/260 3/103	cast iron, PVC, asbestos-cement	aeration
Starogard Lakeland	Tczewskie Laki	692	Cretaceous Tertiary	1/84 1/96	cast iron, steel	aeration, deferrisation
	Tczew-intakes: – Park – Motlawa	65 000	Cretaceous Quaternary-Tertiary Tertiary Cretaceous	3/150-180 5/92-105.5 10/93-110 1/150	cast iron, PVC, asbestos-cement	aeration, deferrisation, manganese removal, biological ammonia removal
	Starogard Gdanski Wierzyca	48 328	Quaternary	8/72-80	cast iron, steel, PVC	aeration, deferrisation
Ilawa Lakeland	Sztum	15 260	Quaternary Tertiary	4/60-80 1/155	cast iron, PVC, asbestos-cement	aeration
	Dzierzgon	7 100	Tertiary	2/168, 175	cast iron, PVC, asbestos-cement	aeration

The analyzed sites were situated in Quaternary formations with a depth of 35–80 m, as well as Tertiary and Cretaceous formations with a depth of 260 m. Water purity was studied in the process of water production, treatment and distribution. In view of the above, the study accounted for the type of piping material applied in a given distribution network. The geological structure of the investigated regions was determined based on the statements on water management conditions supplied by mains operators as well as on hydrological reports of underground water resources of the Polish Geological Institute [10, 11]. The following optical properties of the collected water samples were studied: turbidity – by spectrophotometry at a wavelength of 420 nm [12], color – according to the platinum-cobalt scale [13], iron levels – by spectrophotometry with phenanthroline [14], and manganese levels – by the colorimetric method with persulfate at a wavelength of 525 nm [15]. To compare changes in the physical and chemical composition of water between the point of water intake and the end-user, analytical samples were collected from: the water intake (raw water), treatment station (treated water) and the distribution network (end-user). The average values noted throughout the experimental period were compared with the maximum allowable concentrations (MAC) in view of the characteristic features of monitoring sites in each region (Table 1), including hydrogeological conditions, the applied treatment technology and pipeline material. Those factors were deployed in a statistical analysis to determine the presence of correlations, and in a one-factor analysis of variance (ANOVA) with the use of Duncan's test, at a significance level of $p \leq 0.05$. The results were processed mathematically and statistically with the use of the StatSoft Statistica 7.1 application.

Results

The results of the multi-year study indicate that excessive manganese and iron levels deteriorated the organoleptic properties of water such as turbidity and color. The turbidity of the analyzed samples ranged from 0.0 to 40 NTU, and significant variations were reported both within and between the studied regions, as demonstrated by the coefficients of variation (cv) reaching from 0 % in Male Walichnowy to 181 % in Malbork (Table 2). The highest turbidity was reported in raw water samples from Quaternary deposits in Sztum (28.0 NTU), Starogard Gdanski (15.0 NTU), Zulawy Water Mains – ZWM (26.4 NTU) and Gardeja (14.2 NTU). Monitoring sites were situated in four regions, and the variations in the quality of the collected water samples were due to the specific environmental factors in each studied region. Raw water samples obtained from shallower water-bearing horizons were characterized by poorer optical properties. Increased color values were determined in samples from Quaternary (Q) and Quaternary-Tertiary (QT) horizons, and the maximum allowable concentrations of 15 $mg \cdot dm^{-3}$ Pt were exceeded in selected sites. The above applies to water samples from Sztum with an average color value of 28.0 $mgPt \cdot dm^{-3}$, and from ZWM with an average color value of 24 $mgPt \cdot dm^{-3}$. In both areas, the water mains are supplied from the QT horizon (Table 2).

As shown by the data in Table 1, raw water samples obtained from shallower water-bearing horizons (at a depth of around 30 m) were characterized by less satisfactory optical properties, mainly due to the high concentrations of iron and manganese compounds which affected both water turbidity and color. Underground water samples contained organic iron, and total Fe concentrations ranged from 0.05 to 6.9 $mg \cdot dm^{-3}$. Average total Fe levels were determined in the range of 0.11 $mg \cdot dm^{-3}$

Table 2

Statistical characteristics of the turbidity and color parameters of raw water samples collected from selected intakes in the Ilawa Lakeland, Starogard Lakeland, Vistula Zulawy and the Lower Vistula Valley in 1990–2004

Mesoregion	Intake	Turbidity [NTU]				Color [mgPt · dm^{-3}]			
		Mean	Min	Max	*cv* [%]	Mean	Min	Max	*cv* [%]
Ilawa Lakeland	Dzierzgon	6.5	0.0	15.0	82	12.0	10.0	15.0	58
	Sztum	28.0	9.0	40.0	49	28.0	15.0	40.0	31
Starogard Lakeland	Starogard Gdanski	6.0	6.0	16.0	83	15.0	7.0	20.0	51
	Tczew	7.0	4.0	10.0	5	4.0	1.0	5.0	26
	Tczewskie Laki	3.2	0.0	5.0	60	4.7	1.0	16.5	109
Vistula Zulawy	Malbork	1.3	0.0	7.0	181	7.0	1.0	13.0	58
	Zulawy Water Mains	26.4	15.0	35.0	24	23.9	20.0	28.0	9
Lower Vistula Valley	Gardeja	14.2	5.0	30.0	65	20.7	12.5	30.0	36
	Gniew	9.4	2.0	19.0	32	5.0	2.0	6.5	35
	Kwidzyn	12.4	7.0	30.0	90	21.1	15.0	25.0	21
	Male Walichnowy	2.0	2.0	2.0	0	2.5	2.0	3.0	28
	Wielkie Walichnowy	2.7	2.0	3.0	21	2.0	1.0	3.0	50

in Malbork to 5.64 mg · dm^{-3} in Sztum. The maximum allowable concentrations (MAC) of iron – MAC_{Fe} = 0.20 mg · dm^{-3} Regulation of the Health Minister of 2007 [16] were exceeded in all raw water samples (excluding Malbork) which required treatment (Table 3).

Table 3

Statistical characteristics of iron and manganese concentrations in raw water samples collected in the Ilawa Lakeland, Starogard Lakeland, Vistula Zulawy and the Lower Vistula Valley in 1990–2004

Mesoregion	Intake	Iron [mg total Fe · dm^{-3}]				Manganese [mgMn · dm^{-3}]			
		Mean	Min	Max	*cv* [%]	Mean	Min	Max	*cv* [%]
Ilawa Lakeland	Dzierzgon	0.42	0.30	0.80	29	0.150	0.080	0.220	67
	Sztum	5.64	2.50	6.90	39	0.280	0.190	0.400	29
Starogard Lakeland	Starogard Gdanski	2.00	1.75	2.40	14	0.190	0.150	0.270	21
	Tczew	0.24	0.10	0.45	38	0.013	0.001	0.040	130
	Tczewskie Laki	0.46	0.20	0.74	4	0.017	0.001	0.080	150
Vistula Zulawy	Malbork	0.11	0.05	0.20	55	0.020	0.000	0.080	150
	Zulawy Water Mains	3.79	3.27	6.23	26	1.220	0.720	1.720	25
Lower Vistula Valley	Gardeja	4.00	2.90	4.90	26	0.260	0.200	0.400	23
	Gniew	0.70	0.30	1.10	51	0.050	0.030	0.060	165
	Kwidzyn	3.55	3.05	4.05	22	0.180	0.140	0.300	83
	Male Walichnowy	0.40	0.10	0.50	58	0.000	0.000	0.000	0
	Wielkie Walichnowy	0.33	0.30	0.40	18	0.001	0.000	0.002	0

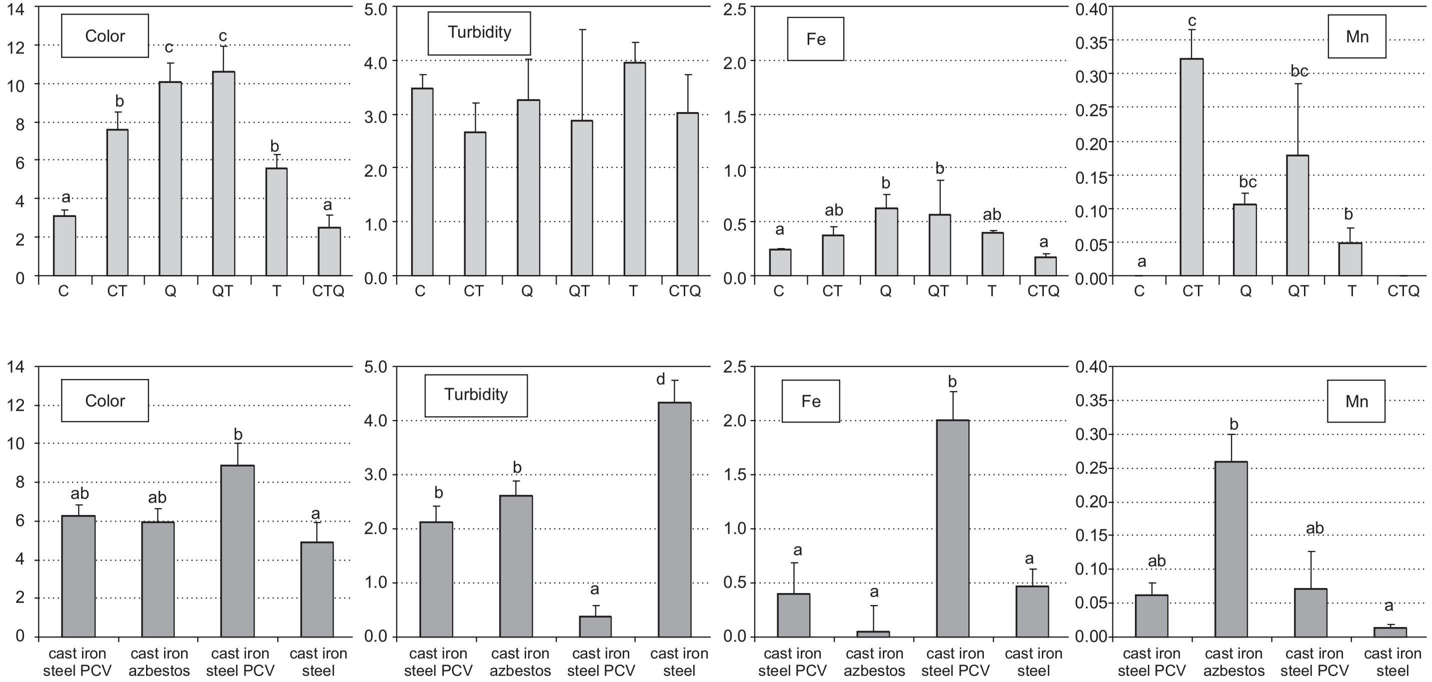

Fig. 1. Changes in color [mgPt · dm^{-3}], turbidity (NTU), total iron and manganese contents [mg · dm^{-3}] in raw water samples, subject to the water-bearing horizon (C – Cretaceous, T – Tertiary, Q – Quaternary) and in the treated water samples, subject to the applied pipeline material. Vertical ranges indicate the standard error of the mean (+SE). Identical letters (a, b) indicate groups of homogenous means (that do not produce significant differences in Duncan's test, ANOVA, post-hoc, $p < 0.05$)

The maximum allowable concentrations of manganese in raw water samples were exceeded in selected monitoring sites in every studied region [9]. The highest manganese levels between 0.72 and 1.72 mg $\cdot$ dm^{-3} were reported in ZWM (Table 3). Manganese concentrations reached from 0.19 to 0.40 mgMn $\cdot$ dm^{-3} in Sztum, and from 0.14 to 0.30 mgMn $\cdot$ dm^{-3} in Kwidzyn. The lowest manganese levels were determined in raw water samples from Male Walichnowy, Wielkie Walichnowy, Tczew, Tczewskie Laki and Malbork.

The characteristic features of the studied raw water samples were mirrored by the results of statistical analyses carried out with the use of Duncan's test at $p \leq 0.05$ (Fig. 1). Test results indicate that raw water samples collected from Cretaceous, Tertiary and Quaternary (CTQ) horizons formed a statistically homogenous group with the lowest iron concentrations (a) in comparison with Quaternary (b) and Tertiary--Quaternary (c) horizons.

The highest correlations were determined between the turbidity of raw water samples and their iron ($r = 0.83$) and manganese ($r = 0.54$) content. The effect of color on water turbidity ($r = 0.71$) was also accounted for in the evaluation of raw water quality.

The applied treatment methods alter the chemical composition and the optical properties of water. In selected monitoring stations, treatment minimized the level of pollutants which affect water color, and the relevant reduction ranged from 17 % in Kwidzyn to 63 % in Starogard Gdanski. In several sites, including Wielkie Walichnowy, Male Walichnowy and Tczewskie Laki, treatment enhanced water color (Table 4). The above was attributed to the type of pipeline material (cast iron, steel) and the condition of the distribution network.

Table 4

Statistical characteristics of the turbidity and color parameters of treated water samples collected in the Ilawa Lakeland, Starogard Lakeland, Vistula Zulawy and the Lower Vistula Valley in 1990–2004

Mesoregion	Intake	Turbidity [NTU]				Color [mgPt $\cdot$ dm^{-3}]			
		Mean	Min	Max	*cv* [%]	Mean	Min	Max	*cv* [%]
Ilawa Lakeland	Dzierzgon	2.2	0.0	5.0	81	5.0	1.0	10.0	72
	Sztum	1.2	0.0	5.0	174	11.1	3.0	18.0	39
Starogard Lakeland	Starogard Gdanski	1.7	1.0	3.0	32	5.5	3.0	10.0	47
	Tczew	0.2	0.0	1.0	70	2.1	1.0	2.5	47
	Tczewskie Laki	3.2	0.0	5.0	57	6.8	4.0	16.5	83
Vistula Zulawy	Malbork	0.7	0.0	5.0	140	8.6	5.0	15.0	44
	Zulawy Water Mains	1.5	0.0	3.0	82	12.6	5.0	17.0	34
Lower Vistula Valley	Gardeja	1.0	0.0	1.0	97	9.7	5.0	20.0	46
	Gniew	3.9	2.0	5.0	35	3.4	2.0	5.0	30
	Kwidzyn	0.2	0.0	1.5	152	17.5	5.0	30.0	39
	Male Walichnowy	3.1	1.0	5.0	57	3.0	1.0	5.0	40
	Wielkie Walichnowy	1.6	0.0	5.0	49	2.7	2.0	5.0	46

The above could be due to the applied treatment method which involved mostly water aeration (deferrization was used additionally only in Tczewskie Laki). The effectiveness of treatment in minimizing water turbidity could suggest a high content of dissolved humus compounds which were relatively easily decomposed.

Water treatment involves the removal of iron and manganese, although in raw water, manganese is found in much lower concentrations than iron. In Kwidzyn, water turbidity was effectively minimized owing to the use of a treatment method that involved deferrization.

The majority of raw water samples required treatment to remove excess iron. In Sztum, average iron concentrations were reduced from 5.64 mg total Fe · dm^{-3} in raw water to 0.18 mg total Fe · dm^{-3} in treated water, and the respective reduction in Gardeja was from 4.00 to 0.10 mg total Fe · dm^{-3}. Iron levels were lowered to the MAC limit of 0.20 mg · dm^{-3} (Table 5) only in selected treatment stations. MAC levels for iron were exceeded in, among others, Dzierzgon (0.37 mg total Fe · dm^{-3}), Starogard Gdanski (0.45 mg total Fe · dm^{-3}), Tczewskie Laki (0.30 mg total Fe · dm^{-3}) and Kwidzyn (0.36 mg total Fe · dm^{-3}).

Table 5

Statistical characteristics of iron and manganese concentrations in treated water samples in the Ilawa Lakeland, Starogard Lakeland, Vistula Zulawy and the Lower Vistula Valley in 1990–2004

Mesoregion	Intake	Iron [mg total Fe · dm^{-3}]				Manganese [mgMn · dm^{-3}]			
		Mean	Min	Max	*cv* [%]	Mean	Min	Max	*cv* [%]
Ilawa Lakeland	Dzierzgon	0.37	0.20	0.50	21	0.015	0.070	0.150	153
	Sztum	0.18	0.04	0.30	72	0.100	0.040	0.160	57
Starogard Lakeland	Starogard Gdanski	0.45	0.10	0.80	90	0.069	0.170	0.200	117
	Tczew	0.10	0.03	0.20	83	0.000	0.000	0.003	143
	Tczewskie Laki	0.30	0.20	0.50	47	0.002	0.000	0.005	110
Vistula Zulawy	Malbork	0.10	0.05	0.22	70	0.010	0.000	0.040	200
	Zulawy Water Mains	0.20	0.03	0.35	68	0.200	0.010	0.400	4
Lower Vistula Valley	Gardeja	0.10	0.06	0.30	122	0.145	0.020	0.180	80
	Gniew	0.23	0.09	0.80	76	0.018	0.000	0.038	0
	Kwidzyn	0.36	0.05	1.20	108	0.078	0.010	0.118	7
	Male Walichnowy	0.20	0.10	0.85	68	0.000	0.000	0.000	0
	Wielkie Walichnowy	0.23	0.15	0.30	31	0.001	0.000	0.003	300

The correlations between the parameters of treated water samples were lower than between those of raw water samples. The above seems to be an obvious conclusion as pollutants are eliminated in the treatment process. Water treatment could also affect the concentrations of compounds that cause turbidity at the point of intake. The value of the correlation coefficient r = –0.46 also provides indirect evidence that the turbidity of treated water decreases over time. The depth of water-bearing horizons had a significant influence on treatment efficiency as regards turbidity parameters (r = –0.25). Physical and chemical factors had a negligent effect on the total iron content of treated water samples. The above results are not surprising since the physical and chemical composition of water was actively modified in the treatment process.

The flow of water via the distribution network affects water quality parameters which vary subject to the size and the length of mains pipeline, the speed with which water reaches the end-user, and the applied construction material. The chemical composition of water distributed via the network is an important consideration as it guarantees its chemical stability. Water quality can affect the network and vice versa, and this fact is always reflected in the quality of water supplied to end-users. The above is illustrated by selected color and turbidity parameters as well as iron and manganese concentrations in samples of mains water, as shown in Tables 6 and 7. In Kwidzyn, the color of mains water samples was enhanced in comparison with the samples collected from the treatment station, resulting in an increase from 17.5 mgPt · dm^{-3} to 22.0 mgPt · dm^{-3}, respectively. Similar results were noted in Dzierzgon, where an increase of 140 % was reported, as well as in Wielkie Walichnowy (51.8 %). The above results were clearly affected by the turbidity of mains water. As regards Zulawy, the average values were in the range of 0.2 NTU to 0.6 NTU (Table 6).

Table 6

Statistical characteristics of the turbidity and color parameters of mains water samples collected in the Ilawa Lakeland, Starogard Lakeland, Vistula Zulawy and the Lower Vistula Valley in 1990–2004

Mesoregion	Intake	Turbidity [NTU]				Color [mgPt · dm^{-3}]			
		Mean	Min	Max	*cv* [%]	Mean	Min	Max	*cv* [%]
Ilawa lakeland	Dzierzgon	2.5	0.0	5.0	100	10.2	3.0	12.0	56
	Sztum	2.5	0.0	10.0	86	7.8	5.0	10.0	37
Starogard Lakeland	Starogard Gdanski	5.5	5.0	6.0	15	5.3	4.0	6.0	8
	Tczew	0.4	0.4	1.0	77	1.8	1.0	2.5	53
	Tczewskie Laki	2.4	0.5	8.0	103	3.6	3.0	4.0	40
Vistula Zulawy	Malbork	0.2	0.0	1.0	240	5.5	0.0	10.0	60
	Zulawy Water Mains	0.6	0.0	3.0	168	11.1	6.0	15.0	24
Lower Vistula valley	Gardeja	1.0	0.0	2.0	200	9.5	5.0	15.0	37
	Gniew	3.2	1.0	5.0	59	3.7	1.0	5.0	46
	Kwidzyn	0.8	0.0	2.0	230	22.0	14.0	30.0	32
	Male Walichnowy	2.9	2.0	5.0	37	3.2	2.0	5.0	40
	Wielkie Walichnowy	2.5	1.1	5.0	54	4.1	1.0	11.0	75

Water turbidity was also within safe levels in Tczew (0.4 NTU) and Kwidzyn (0.8 NTU). In the remaining distribution networks, average turbidity parameters exceeded the allowable norm. In many sites, the flow of water via the network had a negative effect on water quality, as shown by an increase in the turbidity of mains water samples in comparison with the samples collected from treatment stations in Dzierzgon, Sztum, Starogard Gdanski and Wielkie Walichnowy (Table 6).

The increase in turbidity parameters resulting from pipeline flow ranged from 14 % in Dzierzgon to 224 % in Starogard Gdanski. Although the turbidity of water samples collected in Kwidzyn was within the norm (0.8 NTU), the turbidity of water supplied to the end-user increased by 300 % on average, in comparison with water samples obtained from the treatment station (0.2 NTU).

An analysis of water supplied to end-users indicate that iron concentrations were also elevated in selected monitoring points. In comparison with the average iron content of water samples collected from treatment stations, the highest increase of 350 % was noted in the water mains in Gardeja, followed by Malbork (110 %), Sztum (78 %) and Tczew (50 %). In Tczew, the maximum allowable concentrations of iron were not exceeded despite the above increase. The iron content of water supplied to end-users decreased only in ZWM and Dzierzgon (Table 7).

Table 7

Statistical characteristics of iron and manganese concentrations in mains water samples collected in the Ilawa Lakeland, Starogard Lakeland, Zulawy and the Lower Vistula Valley in 1990–2004

Mesoregion	Intake	Iron [mg total Fe $\cdot$ dm^{-3}]				Manganese [mgMn $\cdot$ dm^{-3}]			
		Mean	Min	Max	*cv* [%]	Mean	Min	Max	*cv* [%]
Ilawa lakeland	Dzierzgon	0.33	0.20	0.50	30	0.079	0.030	0.100	28
	Sztum	0.32	0.02	0.40	8	0.093	0.040	0.160	14
Starogard Lakeland	Starogard Gdanski	0.50	0.20	1.14	60	0.073	0.030	0.100	60
	Tczew	0.15	0.02	0.20	47	0.002	0.000	0.010	108
	Tczewskie Laki	0.31	0.22	0.52	32	0.005	0.000	0.030	220
Vistula Zulawy	Malbork	0.21	0.08	0.30	71	0.020	0.000	0.040	100
	Zulawy Water Mains	0.16	0.01	0.60	56	0.130	0.020	0.400	100
Lower Vistula valley	Gardeja	0.45	0.03	0.75	157	0.145	0.050	0.430	142
	Gniew	0.29	0.10	0.40	58	0.034	0.031	0.055	130
	Kwidzyn	0.42	0.10	1.70	88	0.110	0.050	0.180	200
	Male Walichnowy	0.25	0.10	0.90	52	0.001	0.000	0.002	0
	Wielkie Walichnowy	0.25	0.10	0.45	42	0.002	0.000	0.006	0

Mains distribution had a varied effect on changes in the manganese content of water. The greatest variations were noted in sites with elevated manganese concentrations in raw and treated water, excluding the Zulawy Water Mains where the allowable concentrations of manganese were exceeded in all water types. Unexpected results were reported in Dzierzgon where manganese levels increased more than five-fold from 0.015 mgMn $\cdot$ dm^{-3} in treated water samples to 0.079 mgMn $\cdot$ dm^{-3} in mains water (Table 7). A lower, yet statistically significant increase was also observed in mains water in Kwidzyn (89 %). The above could be attributed to the condition of the distribution network – despite the significant impact of pipeline material ($r = 0.24$), the material applied in Dzierzgon and Kwidzyn networks was similar to that used in other monitoring sites (Table 1).

The color of mains water did not differ significantly from that reported in treated water samples. Despite the above, a significant correlation was noted between color and pipeline material (r = 0.21). This trend is illustrated in Table 5.

The results of analyses carried out between 1990 and 2004 point to significant correlations between the studied parameters affecting water quality in the distribution network. Such correlations were noted between water turbidity and iron content, as well as between water color and iron content (Fig. 2).

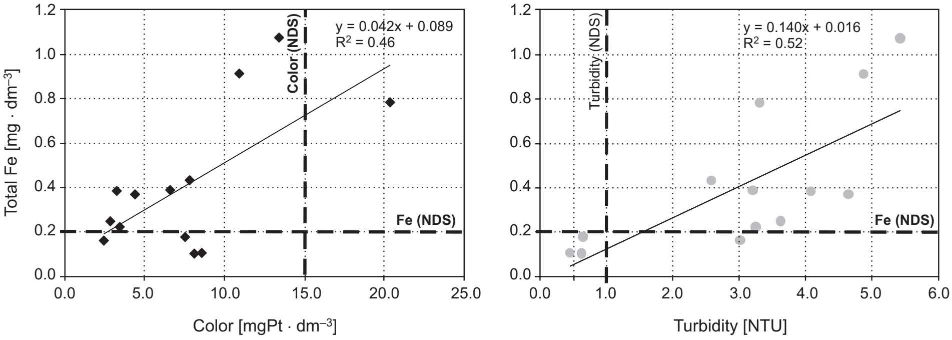

Fig. 2. Correlations between the iron content [mgFe · dm^{-3}] of mains water in the Ilawa Lakeland, Starogard Lakeland, Vistula Zulawy and the Lower Vistula Valley in 1990–2004, water color and turbidity

The flow of water through the distribution network modifies the parameters of treated water to a varied degree. This is an adverse phenomenon, as the final product supplied to end-users may not comply with standard requirements. For this reason, optical parameters and the manganese and iron content of potable water have to be monitored on a regular basis.

Conclusions

1. The optical properties of underground water samples intended for consumption (raw water) and water distributed via the mains network varied significantly due to the presence of iron and manganese.

2. The lowest quality parameters (high total iron and manganese concentrations) were noted in water samples from Quaternary deposits which had a 33 % share of all samples analyzed in the study. The highest iron concentrations were reported in raw water samples from Sztum (2.50–6.90 mg · dm^{-3}), followed by Gardeja (2.90–4.90 mg · dm^{-3}), Zulawy Water Mains (3.27–6.23 mg · dm^{-3}) and Starogard Gdanski (1.75–2.40 mg · dm^{-3}). Excessive manganese levels were observed in raw water samples from Zulawy Water Mains (0.72–1.72 mg · dm^{-3}), Sztum (0.19–0.40 mg · dm^{-3}), Gardeja (0.20–0.40 mg · dm^{-3}) and Starogard Gdanski (0.15–0.20 mg · dm^{-3}).

3. Elevated values of physical and chemical parameters indicate that raw water samples are not fit for direct consumption and require treatment. The average indicator of treatment effectiveness, expressed as the percentage of samples in which MAC

values for a given parameter were exceeded, was 29 % for iron and 22 % for manganese. The percentage of mains water samples in which MAC values were exceeded reached 56 % for iron and 34 % for manganese.

4. The introduction of more stringent treatment criteria led to an improvement in water quality. The turbidity, color, iron and manganese content of treated water was lowered. Yet standard parameters were exceeded in 70 % of the studied sites, indicating that the applied treatment methods are inefficient. Iron (60 %), manganese (40 %) and turbidity (60 %) levels were most significantly exceeded in water samples from the region of the Lower Vistula Valley.

5. Technological factors had a more significant impact on the analyzed parameters of treated and mains water than environmental factors. Although technological processes had a decisive effect on the quality of water supplied to end-users, the majority of the analyzed parameters were correlated with the origin of raw water samples.

6. The results of the study indicate that the mains network in Tczew which supplies the largest population (65,000) was characterized by the most satisfactory hydrogeological conditions, the highest treatment efficiency and the most satisfactory parameters of water supplied to end-users.

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CZYNNIKI WARUNKUJĄCE WŁAŚCIWOŚCI OPTYCZNE WÓD PODZIEMNYCH PRZEZNACZONYCH DO SPOŻYCIA

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Abstrakt: W oparciu o wyniki badań wód podziemnych, przeprowadzonych w latach 1990–2004, określono właściwości optyczne wód (barwa i mętność) oraz stężenie w nich związków żelaza i manganu. Wody pobierano z 12 punktów monitoringowych na ujęciach położonych w regionach: Dolina Dolnej Wisły, Żuławy Wiślane, Pojezierze Starogardzkie i Pojezierze Iławskie. Stwierdzono, że pod względem mętności badane wody surowe nie spełniały obowiązującej normy (1 NTU) i wymagały uzdatniania. O właściwościach optycznych ujmowanych wód decydowały stężenia w nich związków żelaza i manganu. W każdym z regionów występowały również wody zawierające duże ilości żelaza. Zdecydowanie najzasobniejsze w żelazo były wody surowe w ujęciu Sztum (od 2,50 do 6,90 $\text{mgFe}_{\text{og.}} \cdot \text{dm}^{-3}$), a najuboższe w Malborku (od 0,05 do 0,20 $\text{mgFe}_{\text{og.}} \cdot \text{dm}^{-3}$). Zaś największe stężenia manganu (0,72 do 1,72 $\text{mg} \cdot \text{dm}^{-3}$) stwierdzano w wodach surowych Centralnego Wodociągu Żuławskiego. Z kolei w Sztumie wynosiły one od 0,19 do 0,40 $\text{mgMn} \cdot \text{dm}^{-3}$, a w Kwidzynie od 0,14 do 0,30 $\text{mgMn} \cdot \text{dm}^{-3}$. Najmniejsze stężenia manganu występowały w wodach surowych, ujmowanych z pięter wodonośnych Trzeciorzędu i Kredy. Z tego względu wody te nie wymagały uzdatniania.

Kontakt wody z siecią na ogół zmieniał parametry wody uzdatnionej. Nie jest to zjawisko korzystne, bowiem odbiorca może otrzymać produkt niespełniający wymaganych norm. Dlatego tak ważne jest monitorowanie właściwości optycznych wody oraz zawartości w niej żelaza i manganu począwszy od ujęcia, poprzez stację uzdatniania do odbiorcy.

Słowa kluczowe: barwa, mętność, żelazo, mangan, piętra wodonośne, jakość wody

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CONTENT OF HEAVY METALS AND THEIR FRACTIONS IN SOIL IN RESULT OF RESIDUAL EFFECT OF WASTE MATERIALS

ZAWARTOŚĆ METALI CIĘŻKICH I ICH FRAKCJI W GLEBIE W WYNIKU NASTĘPCZEGO ODDZIAŁYWANIA MATERIAŁÓW ODPADOWYCH

Abstract: Analysed was the effect of various material supplements, *ie* municipal sewage sludge and various doses of ash-sludge and ash-peat mixtures on total content of heavy metals (Cr, Zn, Pb, Cu, Cd and Ni) and their fractions. Five fractions of heavy metals were determined in soil by means of Tessier's method after competed three-year pot experiment on maize as the test plant.

Application of ash-sludge and ash-peat mixtures to the soil influenced the increase in heavy metal content in soil but the amount of these metals did not exceed the standards established for arable soils. The pot experiment with maize revealed that the residual fraction played the main role in Cr, Zn and Pb accumulation, fraction bound to organic matter in Cu and Ni accumulation, whereas exchangeable and residual fraction in Cd accumulation. Heavy metal mobility (the sum of two first fractions) in the analysed ash-sludge and ash-peat mixtures supplied to the soil, irrespectively of applied extractant, was diversified and did not exceed the following values of total content: Cr – 0.39 %; Zn – 20 %, Pb – 13 %, Cu 10 %, Cd – 69 % and Ni – 4 %. The investigations have shown that cadmium was the best available to maize whereas chromium the least.

Keywords: municipal sewage sludge, peat, furnace ash, soil, heavy metals, speciation

Introduction

Systematically increasing volume of generated wastes and regulations limiting their storage make waste management a very important ecological, technical and economic

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problem [1–3]. Environmental management of municipal sewage sludge and furnace ashes meets with growing approval owing to their physicochemical properties [4–5].

Municipal sewage sludge after their processing should return to the natural environment because of their content of organic matter and biogenic components. Their environmental application is recommended, particularly for reclamation purposes [2, 6–7]. Environmental management of municipal sewage sludge is usually limited because of their abnormal contents of heavy metals [8]. In case of the abnormal heavy metal content in sewage sludge, their thermal disposal is recommended [1].

Due to their considerable de-acidifying properties, furnace ashes have recently been used for the environment protection and in municipal economy for neutralising acid sewage, which allows for their rational utilisation, at the same time limiting their stored amounts [9]. Furnace ashes are not hazardous wastes, so their environmental utilisation is possible, including reclamation of landfills [10, 11]. However, beside a high content of soil de-acidifying compounds, also trace elements are present in ashes and may pose ecological hazard [12].

When municipal sewage sludge are mixed with furnace ashes, we will obtain a ash-sludge mixture which may be used for reclamation of a landfill site. Owing to its new physicochemical properties, composed ash-sludge mixture may contain heavy metals in various forms [4, 6]. Therefore, an attempt was made at an assessment of heavy metal mobility from these wastes after their mixing and application to the soil.

Material and methods

The research on the effect of municipal sewage sludge, furnace ashes, peat and their mixtures on physicochemical soil properties was conducted after the 3-year pot experiment was completed. The test plant in the pot experiment was maize. The effect of the materials mentioned above on macroelement, microelement and heavy metal content in maize was discussed in earlier publications [13–15].

Present paper examined the effect of various material supplements, *ie* municipal sewage sludge, furnace ash and various doses of ash-sludge mixtures on the total content of heavy metals (Cr, Zn, Pb, Cu, Cd and Ni) and their fractions.

In case of abnormal concentrations of heavy metals in sewage sludge, the waste maybe replaced by peat, which does not pose any ecological hazard and at the same time is characterized by similar physicochemical properties [16, 17]. Therefore, also an ash-peat mixture was made to compare the availability and heavy metal mobility from sewage sludge and furnace ash. The ash-peat mixture will also allow to assess potential heavy metal release from furnace ash to which organic matter was added as peat.

Five heavy metal fractions were determined in soil by means of Tessier's method [18] after completed three year pot experiment with maize as the test plant.

Very acid soil used for the experiment had a loamy silt texture (Table 1) containing 26 % of sand, 69 % of silt and 5 % of clay. Regarding the agronomic category, the furnace ash applied in the experiment corresponded to medium loam and regarding the texture to sandy loam [19].

Table 1

Characteristic of physicochemical materials used in experiment

Parameter	Unit	Soil	Sewage sludge	Ash	Peat
Texture		Silt loam	—	Sandy loam	—
$pH_{(KCl)}$	[-]	4.60	6.67	9.85	4.82
$pH_{(H_2O)}$		4.73	6.82	10.06	5.26
Hydrolytic acidity	$[mmol(+) \cdot kg^{-1}]$	70.68	161.96	3.63	831.94
Base exchange capacity		42.45	887.03	260.25	317.09
Organic C	$[g \cdot kg^{-1}]$	18.48	219.16	23.69	370.50
Total N		1.92	35.25	0.53	11.49
Available P	$[mg \cdot kg^{-1}$ d.m.]	57.43	611.40	41.18	269.75
Available K		72.42	247.60	140.33	117.97
Available Mg		109.75	885.49	989.86	999.86
Total Cr		39.33	48.95	33.85	11.55
Total Pb		40.40	59.25	18.65	2.75
Total Cu		8.28	272.25	74.50	1.18
Total Zn		70.25	1182.50	93.75	9.28
Total Cd		0.43	5.10	0.28	0.05
Total Ni		30.08	23.03	39.98	7.30

The experiment was conducted in four replications, in polyethylene pots of 6 kg volume, filled with ash-sludge and ash-peat mixtures in the amount of 1–30 % of the total soil mass. The experimental design comprised also objects obtaining solely the individual components of the mixtures (Table 2). In all pots annual constant NPK fertilization with 0.3 gN, 0.08 gP and 0.2 gK $\cdot$ kg^{-1} of soil in the form of NH_4NO_3, KH_2PO_4 and KCl was applied each year. The mineral fertilizers, as solutions, were applied in the first year, two weeks before plant sowing and were thoroughly mixed with soil. In the second and third year of the experiment the fertilizers were applied in early spring before maize vegetation started. During vegetation the plants were watered with bi-distilled water and the soil moisture was maintained on the level of 60 % maximum water capacity.

When the experiment was finished, total heavy metal content was assessed in the soil after the samples dissolving in a mixture of nitric and perchloric acids (3:2, *v*/*v*) [20] and the metal fractions by Tessier's method [18].

Speciation of heavy metals

The content of various metal fractions in the analysed substrata was determined by means of metal sequential extraction scheme by Tessier et al [18]. Five fractions of heavy metals (Cr, Zn, Pb, Cu, Cd and Ni) were identified:

1. Exchangeable metals, exchangeable fraction (FI) – air dried and homogenized material was extracted with 8 cm^3 1.0 M Mg Cl_2, at pH = 7, by shaking for 1 hour at 25 ^oC;

2. Metals bound to carbonates, carbonate fraction (FII) – the exchangeable form residue extracted by 8 cm^3 1.0 M CH_3COONa, at pH = 5, by shaking constantly for 5 hours at 25 ^oC;

3. Metals bound with iron and manganese oxides, oxide fraction (FIII) – carbonate residue extracted for 5 hours in 20 cm^3 of 0.04 M $NH_2OH \cdot HCl$ dissolved in 25 % CH_3COOH (*v*/*v*) at 96 ^oC, mixing from time to time;

4. Metals bound to organic matter, organic fraction (FIV) – Fe-Mn oxide residue extracted by 3 cm^3 of 0.02 M NHO_3 + 5 cm^3 of 30 % H_2O_2 (*v*/*v*) for 2 hours at 85 ^oC, mixing from time to time, then 3 cm^3 of 30 % H_2O_2 was added at 85 ^oC and all was mixed from time to time. Finally it was shaken with 5 cm^3 3.2 M CH_3COONH_4 in 20 % HNO_3 (*v*/*v*) for 0.5 hour at 25 ^oC;

5. Metal residue bound to silicates, residual fraction (FV) – residue after organic form was hot decomposed with 10 cm^3 of 40 % HF and 2 cm^3 of 70 % $HClO_4$, after slight drying 1 cm^3 of $HClO_4$ was added and heated until white fumes appeared. The residue was dissolved in HCl (1:1, *v*/*v*) and diluted to 100 cm^3.

Extraction of one-gram samples of the substratum was conducted in 50 cm^3 polyethylene extraction thimbles. After each extraction the samples were centrifuged, 3000 xg for 30 min, The extraction residue was rinsed with 8 cm^3 of H_2O, centrifuged again as above and the supernatant was removed. In the filtrates of each replication (pot), Cr, Zn, Pb, Cu, Cd and Ni contents present in individual fractions were assessed by means of ICP-AES method and expressed in percent in relation to its total content.

Statistical computations were conducted using Microsoft Excel 7.0 calculation sheet and Statistica v.7.0. Statistical assessment of individual sources of variability was made using analysis of variance procedure. The significance of differences between the compared means of the analysed features (parameters, indices) was stated on the basis of T Tukey's test at significance level for pot experiments $\alpha \leq 0.01$.

Results

Total content

The soil used for the experiment was characterized by the natural content of Pb, Cu and Cd but elevated concentrations of Cr, Zn and Ni (Table 1) [21]. Assessed heavy metal content was below these elements permissible levels in soils classified for fertilization with sewage sludge [8]. A comparison of heavy metal content in furnace ash to limit numbers suggested by IUNG [21] showed a low content of these elements, except copper (Table 1). Therefore, the content of heavy metals in the ash, as compared with the soil, did not constitute a potential source of metals supplied to the soil. Applied sewage sludge contained higher amounts of heavy metals in comparison with furnace ash, however their content did not exceed permissible values conditioning their environmental utilisation [8].

Table 2

Content of Cr and Zn in soil after experiment [mg · kg^{-1}] and share of heavy metal fractions [%]

Objects*	Cr						Zn					
	Total [mg · kg^{-1}]	Fraction [%]					Total [mg · kg^{-1}]	Fraction [%]				
		FI	FII	FIII	FIV	FV		FI	FII	FIII	FIV	FV
1. Control	34.81	0.12	0.14	0.63	16.51	82.59	52.00	6.82	10.92	18.06	23.25	40.94
2. Sludge	46.06	0.11	0.19	0.88	39.42	59.39	1107.50	6.55	10.23	15.65	33.75	33.82
3. Ash	31.75	0.03	10.51	11.34	12.39	65.74	85.25	0.19	2.16	5.48	17.68	74.49
4. Peat	9.16	0.22	0.08	0.98	13.14	85.58	7.06	2.75	7.41	14.15	61.11	14.57
5. AS	34.23	0.08	0.52	4.96	20.25	74.18	549.25	1.37	3.86	5.62	14.93	74.21
6. AP	22.05	0.07	0.59	4.57	29.17	65.60	44.74	0.53	1.04	2.08	40.02	56.33
7. AS 1 %	33.98	0.09	0.15	0.71	17.07	81.97	51.80	7.87	11.82	22.51	28.92	28.87
8. AS 2 %	34.06	0.11	0.16	0.92	20.25	78.57	55.45	6.41	10.47	18.01	30.22	34.89
9. AS 5 %	35.18	0.12	0.19	0.88	21.66	77.16	66.80	5.04	5.54	12.75	27.73	48.94
10. AS 10 %	36.49	0.13	0.18	1.01	25.84	72.83	80.25	3.08	4.64	10.26	27.92	54.10
11. AS 20 %	37.08	0.14	0.20	1.02	26.68	71.96	106.68	0.57	2.49	6.65	26.24	64.04
12. AS 30 %	38.46	0.15	0.22	1.10	30.74	67.79	120.25	0.31	1.06	3.96	25.35	69.33
13. AP 1 %	34.85	0.10	0.14	0.64	19.08	79.04	60.13	7.05	10.04	18.55	26.26	38.10

Table 2 contd.

Objects*	Cr						Zn					
	Total [mg · kg^{-1}]	Fraction [%]					Total [mg · kg^{-1}]	Fraction [%]				
		FI	FII	FIII	FIV	FV		FI	FII	FIII	FIV	FV
14. AP 2 %	34.39	0.10	0.14	0.69	20.19	77.88	59.18	6.16	9.25	17.61	29.60	37.38
15. AP 5 %	34.32	0.11	0.18	0.82	23.35	74.54	57.75	5.91	5.88	15.29	37.54	35.38
16. AP 10 %	33.67	0.09	0.19	0.90	23.29	74.53	55.00	0.72	6.13	14.12	47.23	31.80
17. AP 20 %	32.09	0.13	0.22	1.01	26.93	70.72	54.25	0.55	4.91	11.23	57.25	26.06
18. AP 30 %	31.57	0.14	0.25	1.10	29.49	68.02	52.23	0.37	2.42	8.66	66.70	21.85
V %**	22.54	34.21	306.42	140.77	29.24	9.21	179.95	84.70	58.88	47.65	42.36	41.49
NRI-LSD$_{(\alpha \le 0.01)}$	6.83	—	—	—	—	—	30.64	—	—	—	—	—

* Objects: 1 – Control; 2 – Sewage sludge; 3 – Ash; 4 – Peat; 5 – AS Ash-Sludge 1:1; 6 – AP Ash-Peat 1:1; 7 – AS Ash-Sludge 1 %; 8 – AS Ash-Sludge 2 %; 9 – AS Ash-Sludge 5 %; 10 – AS Ash-Sludge 10 %; 11 – AS Ash-Sludge 20 %; 12 – AS Ash-Sludge 30 %; 13 – AP Ash-Peat 1 %; 14 – AP Ash-Peat 2 %; 15 – AP Ash-Peat 5 %; 16 – AP Ash-Peat 10 %; 17 – AP Ash-Peat 20 %; 18 – AP Ash-Peat 30 %; ** Variation coefficient.

Table 3

Content of Pb and Cu in soil after experiment [mg · kg^{-1}], and percentage of heavy metal fractions [%]

Objects*	Pb						Cu					
	Total [mg · kg^{-1}]	Fraction [%]					Total [mg · kg^{-1}]	Fraction [%]				
		FI	FII	FIII	FIV	FV		FI	FII	FIII	FIV	FV
1. Control	34.44	5.63	8.06	17.28	29.17	39.86	6.03	2.33	6.72	14.11	50.03	26.81
2. Sludge	56.00	5.91	8.46	12.03	30.67	42.92	258.88	2.45	1.82	4.07	79.42	12.25
3. Ash	14.43	0.33	0.45	9.16	28.30	61.76	71.75	0.39	0.09	4.71	54.99	39.81
4. Peat	2.21	2.06	2.37	8.50	32.32	54.75	0.89	8.70	1.49	9.55	61.03	19.23
5. AS	34.16	0.23	0.30	5.97	24.29	69.20	153.38	4.33	0.75	3.86	59.66	31.40
6. AP	10.10	0.35	1.02	11.28	14.59	72.75	35.00	0.54	0.44	4.04	73.91	21.07
7. AS 1 %	36.51	4.30	6.56	12.91	20.77	55.46	8.10	1.95	4.51	16.03	49.77	27.74
8. AS 2 %	36.58	3.72	6.46	12.58	18.73	58.51	8.21	2.10	6.20	15.05	52.48	24.17
9. AS 5 %	36.00	3.45	5.71	10.51	15.77	64.56	10.70	2.25	5.48	15.06	55.40	21.81
10. AS 10 %	35.91	1.72	2.77	5.29	15.69	74.52	14.36	2.42	5.80	13.18	56.15	22.45
11. AS 20 %	35.89	0.55	2.32	3.91	10.21	83.02	21.20	2.44	7.07	17.55	58.87	14.07
12. AS 30 %	35.38	0.47	1.09	2.47	8.83	87.14	30.23	2.39	6.39	15.72	59.85	15.65
13. AP 1 %	37.89	5.20	7.14	14.85	19.87	52.94	7.84	1.42	4.87	9.68	48.67	35.36
14. AP 2 %	37.08	4.23	6.39	14.18	20.13	55.07	7.85	1.06	4.49	8.27	55.62	30.56
15. AP 5 %	36.66	3.70	5.81	9.91	15.85	64.73	8.30	0.92	2.46	6.29	54.50	35.84
16. AP 10 %	35.49	1.07	2.15	5.93	12.33	78.51	9.18	0.73	1.96	4.71	52.21	40.40
17. AP 20 %	35.19	0.62	1.45	3.76	10.49	83.68	10.41	0.30	1.45	2.63	62.01	33.60
18. AP 30 %	34.68	0.50	1.03	2.49	7.38	88.60	12.54	0.30	1.29	2.45	85.18	10.79
V %***	37.11	83.78	74.19	49.82	41.53	22.25	176.00	95.57	68.91	57.73	17.15	36.11
NRI-LSD$_{(\alpha \leq 0.01)}$	2.75	—	—	—	—	—	3.34	—	—	—	—	—

* Explanations: see Table 2.

Table 4

Content of Cd and Ni in soil after experiment [mg · kg^{-1}] and share of heavy metal fractions [%]

Objects*	Cd						Ni					
	Total [mg · kg^{-1}]	Fraction [%]					Total [mg · kg^{-1}]	Fraction [%]				
		FI	FII	FIII	FIV	FV		FI	FII	FIII	FIV	FV
1. Control	0.34	47.80	5.38	8.96	13.59	24.27	24.99	2.79	0.26	10.42	65.25	21.28
2. Sludge	4.91	19.83	8.35	9.09	10.43	52.31	17.88	6.54	2.07	7.46	64.27	19.67
3. Ash	0.25	3.27	4.90	14.29	26.53	51.02	30.25	0.08	0.05	9.70	65.79	24.37
4. Peat	0.04	25.14	15.69	1.00	25.49	32.68	6.04	3.47	0.59	12.87	59.82	23.25
5. AS	2.13	0.79	1.28	8.38	8.49	81.05	28.78	0.39	0.13	6.55	62.73	30.19
6. AP	0.13	7.21	12.01	12.01	31.23	37.54	20.94	0.23	0.22	11.47	63.56	24.53
7. AS 1 %	0.40	43.17	6.40	6.66	12.13	31.65	24.85	2.17	0.20	10.20	66.23	21.21
8. AS 2 %	0.41	38.57	5.28	5.28	12.88	37.98	24.88	2.02	0.15	8.83	67.93	21.07
9. AS 5 %	0.43	34.41	3.99	4.99	12.97	43.64	25.11	1.72	0.15	6.59	68.06	23.49
10. AS 10 %	0.49	28.38	3.55	4.43	15.13	48.50	25.24	1.40	0.13	5.12	69.44	23.90
11. AS 20 %	0.53	25.15	2.43	2.03	17.14	53.25	25.30	0.94	0.11	3.87	70.58	24.50
12. AS 30 %	0.65	13.04	1.00	1.67	18.47	65.82	25.45	0.64	0.06	2.62	72.23	24.46
13. AP 1 %	0.36	55.70	12.75	10.07	13.09	8.39	25.09	3.12	0.23	11.41	71.01	14.23
14. AP 2 %	0.36	52.53	10.65	10.65	17.30	8.87	24.54	3.20	0.24	7.82	71.36	17.37
15. AP 5 %	0.35	48.85	8.14	13.57	20.95	8.48	24.21	3.09	0.18	7.63	73.92	15.18
16. AP 10 %	0.34	35.54	4.35	18.13	30.64	11.33	24.05	0.82	0.19	5.77	77.00	16.22
17. AP 20 %	0.33	32.53	2.77	19.03	34.86	10.81	24.03	0.75	0.18	4.12	78.30	16.66
18. AP 30 %	0.31	25.31	2.98	26.06	43.56	2.09	23.86	0.20	0.07	2.98	82.43	14.32
V %***	160.56	55.52	67.69	68.96	47.92	66.65	21.51	88.20	159.29	40.98	8.44	21.19
NRI-LSD$_{\alpha \le 0.01)}$	0.17	—	—	—	—	—	2.28	—	—	—	—	—

* Explanations: see Table 2.

The content of Cr, Zn, Pb, Cu and Cd in the applied sewage sludge (object 2), after maize vegetation finished was respectively by 0.32, 21, 0.62, 42 and 14-fold higher in comparison with the control (object 1). Higher content of these heavy metals in sewage sludge affected increase in the metal concentrations in the ash-sludge mixtures added to the soil (objects 7–12).

When ash-sludge mixture was solely applied (object 5), over 10, 25 and 6-fold higher content of Zn, Cu and Cd was assessed in comparison with the control (object 1). On the other hand Cr, Pb and Ni content in ash-sludge mixture was approximate to the content in the control soil.

After three years of maize vegetation increase in Cr, Zn, Cu and Cd content in soil was registered under the influence of ash-sludge mixtures proportion (objects 7–12), whereas Pb and Ni content remained on a similar level (Table 2–4). Insignificant changes in Pb and Ni content in the soil fertilized with ash-sludge mixtures one may explain by low lead content in ash and Ni in sewage sludge (Table 2–4). A significant increase in Cr, Zn, Cu and Cd content in the soil fertilized with ash-sludge mixtures has been explained as due to a their higher content in sewage sludge as compared with their content in soil. Moreover, the source of copper in these objects was also furnace ash. Copper concentration in the furnace ash on which maize was grown was over 11-fold higher as compared with the control soil.

In effect of growing proportions of ash-peat mixtures (objects 13–18) a systematic decline of Cr, Zn, Pb, Cd and Ni content in soil was observed, but a marked increase in Cu content in these substrata. A regular decrease in Cr, Zn, Pb, Cd and Ni concentrations in ash-peat mixtures added to the soil was due to low content of these elements in the used peat. Concentrations of Cr, Zn, Pb, Cu, Cd and Ni in peat (object 4) were over 2.8, 6.4, 14.6, 5.8 and 8.0-fold lower in comparison with the control. Presented research has demonstrated that due to its low content of heavy metals peat used in the ash-peat mixtures could be use as organic matter source in reclaimed substrata.

Heavy metal fractions in soil

Percentage distribution of heavy metals among the separated fractions depended on the analysed element and the kind and dose of the material (Table 2–4). In the control soil after 3 years of maize vegetation, the highest share of Cr, Zn and Pb was revealed in the residual fraction (F V), while Cu and Ni in the fraction bound to organic matter (F IV) and Cd bound to the exchangeable (F I) and residual (F V) fraction (Table 2–4). Among heavy metals in the control soil, the lowest share in the most mobile fractions, *ie* available to plants (fractions F I and F II) was registered for Cr, which did not exceed 0.26 % of total Cr. The biggest share in the most mobile fractions, which exceeded over 50 % of its content, was noted for Cd.

After a 3-year maize cultivation on sewage sludge (object 2) a small quantity of Cr was found also in the mobile fractions and the sum of two first fractions did not exceed 0.30 % of the total content. In object 2, where solely sewage sludge was applied, the biggest amounts of Cr, Zn, Pb and Cd were assessed in the residual fraction (F V), whereas Ni and Cu in the organic fraction (F IV). Copper was most strongly bound by organic matter in the sludge (about 80 %), whereas the highest concentration of Cd, about 52 % was determined in the residual fraction and exchangeable fraction (about 20 %).

In the object where only ash was used (object 3) metals, such as Cr, Zn, Pb and Cd were present mainly in the residual fraction (F V) and Cd and Ni mainly in the organic fraction (over 54 % and 65 %). The best heavy metal availability from furnace ashes (presence in the mobile fractions, F I and F II sum) was assessed for Cr and Cd. It exceeded 10 and 8 % of the total content, respectively. The other analysed metals, such as Zn, Pb, Cu and Ni in most mobile fractions occurred in ash only in small amounts. The content of Zn, Pb, Cu and Ni in F I and F II fractions constituted over: 2.35 %, 0.78 %, 0.49 % and 0.13 % of the total content, respectively. Investigations have demonstrated that furnace ashes to the least extent accumulated Ni and Cu in the mobile fractions (sum of F I and F II). Organic matter (F IV) present in ash as remains of unburnt coal, contributed most to Pb, Cu, Cd and Ni binding and constituted over 28 %, 54 %, 26 % and 65% of its total content, respectively.

In the object where only peat was applied (object 4), heavy metals such as Zn, Cu and Ni occurred mainly in the organic fraction (F IV), whereas the content of Cr, Cd and Pb was registered mainly in the residual fraction (F V). In peat, the biggest share in the most mobile fractions, *ie* available to plants (sum of F I and F II fractions), exceeding 40 % of the total content was assessed for Cd. A considerable proportion in the mobile fractions was found also for Cu and Zn. It exceeded 10 % of their total content.

Ash-sludge (object 5) and ash-peat (object 6) mixtures accumulated the biggest quantities of Cr, Zn, Pb and Cd in the residual fraction (F V), Cu and Ni in the organic fraction (F IV). No considerable share of Cr, Zn, Pb, Cu or Ni in the mobile fractions (sum of F I and F II) was observed in the mixtures mentioned above. The research has shown that ash-peat mixture was a source of Cd in the most mobile fractions, *ie* available to plants where this element share reached about 20 % of the total content.

Under the influence of increasing proportion of ash-sludge mixtures in soil (objects 7–12) a regular increase in Cr and Cu in the most mobile fractions (F I and F II), in the fraction bound to Fe-Mn oxides and in the organic fraction (F III and F IV) was registered. The latter fraction provided a potential source of these metals for maize. On the other hand, presence of Cr and Cu in the residual fraction (F V, almost unavailable to plants) revealed a declining tendency. For Zn and Pb an opposite dependency was registered, *ie* it was found that ash-sludge mixtures added to the soil (object 7–12) caused a systematic decrease in these metals share in the fractions available to plants (F I–F IV), but increase in their content in the residual fraction. Ash-sludge mixtures applied to the soil affected a decrease in Cd and Ni occurrence in F I–F III fractions, whereas these metals share in the organic (F IV) and residual fraction (F V) was growing systematically.

Ash-peat mixtures applied to the soil (objects 13–18) caused an increase in the share of Cr in the phytoavailable fractions (F I and F II), in the fraction bound to Fe-Mn oxides and organic fractions (F III and F IV), whereas this metal percentage in the residual fraction was declining regularly. It was observed that increasing shares of ash-peat mixtures in soil (objects 13–18) caused a decrease in the percentage of Zn, Cu and Ni in the best available to plants fractions (F I–F III) and in the residual fraction (F V), whereas an increase in the percentage of these metals in the organic fraction (F IV) was registered. Increasing share of ash-peat mixtures in soil caused a decreased share of Pb in the phytoavailable fractions (F I–F III) and in the oxide and organic fractions (F III and F IV), whereas their increased share in the residual fraction (F V) was noted. Cd percentage in the most mobile fractions (F I and F II) was systematically decreasing under the influence of increasing share of ash-peat mixtures in the soil (objects 13–18).

Summing up, it was found that the residual fraction (F V) had greatest share in Cr, Zn and Pb accumulation, while the fraction bound to organic matter (F IV) in Cu and Ni and Cd accumulation was most affected by the exchangeable (F I) and residual (F V) fractions.

Mobility of heavy metals (the sum of the first two fractions) in the soil with ash-sludge and ash-peat mixtures (objects 7–12 and 13–18) was diversified and did not exceed Cr – 0.39 %, Zn – 20 %, Pb – 13 %, Cu – 10 %, Cd – 69 % and Ni – 4 % of their total contents. Investigations have demonstrated that the cadmium was the best and chromium the least available to maize.

Discussion

Heavy metal content in the soil, sewage sludge, furnace ashes and peat was greatly diversified, as confirmed by the other authors' research [22, 23]. Diversified content of heavy metals in the analysed materials indicates a necessity for analysing these materials prior to their environmental management. Research of Tipping et al [24] confirms also a considerable distribution of heavy metals in natural peats.

In the opinion of many authors total heavy metal content is not the proper indicator of element availability to plants, it does not inform about potential element mobility in the environment [25, 26]. Although the total content of heavy metals is a commonly used indicator of the degree of pollution of the environment elements (soil, sewage sludge, ash, peat), still it does not determine the real risk of their effect upon the natural environment [3, 8].

According to the quoted authors and Swietlik and Trojanowska [27], while determining phytoavailability, the chemical forms of metals are more important than their total content. Identification of heavy metal chemical forms allows not only for a better characteristics of wastes, but also for a more precise assessment of an element phytoavailability after its supply to the soil. Investigations of Bojarska and Bzowski [28, 29] confirmed that furnace ashes are characterised by a small share of heavy metals in the phytoavailable fractions, particularly Pb and Zn in mobile forms, best available to plants.

A small quantity of Cr assessed in sewage sludge in the most mobile fractions was confirmed by the research of Czekala et al [30]. These authors revealed that even tannery sludge – greatly abundant in chromium, shows very small amount of this element in the water soluble and exchangeable form; its content constituted between 0.05 % and 0.14 % Cr in relation to its total content. Also Piotrowska and Dudka [31] found trace amounts of Cr in the exchangeable fraction extracted from sewage sludges, at the same time revealing that the greatest amount of this element occurred in the "residue" fraction.

Research of many authors confirmed that applied ash-sludge and ash-peat mixtures affect a decrease in heavy metal share in mobile fractions, best available to plants. Decreasing heavy metal availability is connected with the increase in soil pH in result of poorer solubility of minerals and increased absorption by negatively charged colloidal soil particles [29]. Also investigations of Kalembasa and Wysokinski [32] demonstrated that brown and hard coal ash supplement to sewage sludges influences a decrease in Zn and Cu availability to plants. Research conducted by Tipping et al [24] also confirm that application of peats in chemically polluted areas may be used for heavy metal binding.

Conclusions

1. In result of furnace ashes and sewage sludge, peat and their mixtures supply to soil, changes were registered in heavy metals concentrations in the soil.
2. Municipal sewage sludge provided the greatest source of heavy metals present in the best phytoavailable fractions (F I and F II), whereas furnace ash contained the smallest amounts of heavy metals occurring in the fractions available to plants.
3. In result of sewage sludge mixing with furnace ash and peat with furnace ash, a decrease in the quantity of heavy metals occurring in the fractions best available to plants was observed. The higher the share of ash in the ash-sludge mixture, the smaller the share of metals in the phytoavailable forms.
4. Supplying increasing amounts of ash-sludge and ash-peat mixtures to soils generally caused increased Cr concentrations in fractions best available to plants (F I and F II), whereas the share of Zn, Pb, Cu, Cd and Ni in these fractions was declining systematically.
5. A prerequisite for the environmental management of ash-sludge and ash-peat mixtures should be monitoring research conducted on the content of heavy metals in the forms most mobile in the environment.

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ZAWARTOŚĆ METALI CIĘŻKICH I ICH FRAKCJI W GLEBIE W WYNIKU NASTĘPCZEGO ODDZIAŁYWANIA MATERIAŁÓW ODPADOWYCH

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Abstrakt: Badano wpływ dodatku materiałów, tj. komunalnego osadu ściekowego, popiołu paleniskowego i torfu oraz różnych dawek mieszanin popiołowo-osadowych i popiołowo-torfowych na całkowitą zawartość metali ciężkich (Cr, Zn, Pb, Cu, Cd, Ni) oraz ich frakcje. Oznaczono pięć frakcji metali ciężkich w glebie metodą Tessiera po zakończonym trzyletnim doświadczeniu wazonowym z kukurydzą jako rośliną testową.

Zastosowanie do gleby mieszanin popiołowo-osadowych oraz popiołowo-torfowych spowodowało zwiększenie zawartości metali ciężkich w glebie, ale zawartość tych metali nie przekraczała standardów ustalonych dla gleb uprawnych. W doświadczeniu wazonowym z kukurydzą stwierdzono, że główną rolę w magazynowaniu Cr, Zn i Pb odegrała frakcja rezydualna, a Cu i Ni frakcja związana z materią organiczną, natomiast Cd frakcja wymienna i rezydualna. Mobilność metali ciężkich (suma pierwszych dwóch frakcji) w badanych mieszaninach popiołowo-osadowych i popiołowo-torfowych wprowadzonych do gleby, niezależnie od zastosowanego ekstrahenta była zróżnicowana i w przypadku Cr nie przekraczała 0,39 %, Zn – 20 %, Pb – 13 %, Cu – 10 %, Cd – 69 %, Ni – 4 % zawartości ogólnych. Z badań wynika, że największą dostępnością dla kukurydzy odznaczał się kadm, a najmniejszą chrom.

Słowa kluczowe: komunalne osady ściekowe, torf, popioły paleniskowe, gleba, metale ciężkie, specjacja

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EFFECT OF ROOK FAECES ON HEAVY METALS CONTENT IN SOIL AT NESTLING SITES

WPŁYW KOLONII LĘGOWYCH GAWRONA NA ZAWARTOŚĆ METALI CIĘŻKICH W GLEBIE

Abstract: The content of Cu, Fe, Zn, Cd and Pb in rook faeces from two colonies roosting in urban parks in Eastern Poland (Siedlce and Biala Podlaska) and the effect of the colonies upon the metals content in soil were analyzed. The analysis was carried out by comparing the chemical composition of soils at the nestling sites and at the control sites. Differences showed in metals content in the faeces depended on the localization of colonies. The colony from the former site significantly contributed to the content of Cu, Fe, Zn and Cd in soil. Neither of the rook colonies affected soil Pb levels. The chemical composition of rook faeces reflected the quality of the environment in which rooks feed. Our study findings show that the rook is particularly sensitive to local changes in metals content in the environment.

Keywords: rook, breeding colonies, faeces, soil, heavy metals, contamination, bioindicators

Introduction

Birds are used as bioindicators of heavy metal pollution of the environment, for which purpose both feathers [1–4] and bird eggs [5–7] and tissues (liver, lung, kidney, muscle and bone) [8–10] are examined. Numerous reports also recognize the potential of bird faeces as indicators of environmental contamination with trace metals [3, 11–15]. Bioindicative studies frequently use colonial birds. It must be emphasized that birds living in large colonies contribute towards the changes of soil properties caused by deposited bird excrement [4, 12, 14, 15].

There are relatively numerous data regarding water bird colonies contaminating soil with heavy metals [4, 7, 11, 12, 15]. Urban synanthropic birds, however, have been

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examined much more rarely [1, 2]. Among land birds, the rook (*Corvus frugilegus*) is often found roosting in urban parks. In spite of nesting in bigger villages and towns, the rook is strongly associated with open farmland, especially in Eastern Poland [16]. It is an omnivorous, opportunistic feeder with a broad diet and varied nutrient proportions mainly based on *Coleoptera* and cereal grains that are found in the arable fields [17, 18]. The decrease in the rook population in Europe could be the effect of the environment contamination with pesticides and heavy metals [19]. There are few reports concerning the impact of environment contamination on the rook and, on the other hand, the influence of the rook colonies on soil composition. Some authors dealt with the influence of *Corvus frugilegus* on organic matter and N and P contents in soils [20]. The latest study regarding the accumulation of metals in the tissues of the rook nesting in Eastern Poland (Siedlce and its vicinity) was carried out by Orłowski et al. [9, 10] and it indicated that high level of Cd and Pb in the rook tissues may result from its diet. The quality of the bird diet is also reflected in the chemical content of its faeces [11, 15].

Our studies focused on two rook colonies roosting in agricultural region of Eastern Poland: in Siedlce and Biala Podlaska. We analysed the concentrations of Fe, Cu, Zn, Cd and Pb in the rook faeces and determined the influence of the colonies on heavy metals contents in nestling soil samples. We hypothesized that the impact of the rook colonies on the quality of soils and the content of heavy metals in them is alike, irrespective of nests location.

Material and methods

Study area

The study area is situated in the macroregion of the South Podlasie Lowland in eastern Poland. The research included two breeding colonies of the rook inhabiting two urban parks in Biala Podlaska (52^{o}02″N, 23^{o}02″E) and Siedlce (52^{o}10″N, 22^{o}18″E). Both towns lay in an agricultural region within about 70 km of each other. The total area of Biala Podlaska equals 49.4 km^2 and its population is 58 000. Siedlce covers the area of 32 km^2 and its population is 77 000. In Siedlce there are some large industrial plants specializing in metal sector (*eg* a galvanizing plant), whereas no similar ones operate in Biala Podlaska. An international arterial road E2 (Berlin–Moscow) and a major railway route are located in the close vicinity of the two towns.

The urban park in Biala Podlaska is located at the area of about 6 ha. The research focused on its southern part where 224 nests of the rook were found. The tree stand in the park, mainly represented by maple tree (*Acer platanoides*), European ash (*Fraxinus Excelsior*), horse-chestnut (*Asculus hippocastanum*), common alder (*Alnus glutinosa*) and common hornbeam (*Carpinus betulus*), comprises about 60 % of the park area. The park undergrowth comprises about 10 % and the lawns about 30 % of the whole area. In the studied north-eastern part of the park in Siedlce (with the total area of about 11 ha) there were 736 rook nests found. About 80 % of the terrain is covered with the tree stand mainly represented by white elm (*Ulmu leavis*), horse-chestnut (*Asculus hippocastanum*), European ash (*Fraxinus Excelsior)* and small-leaf line (*Tilia cordata*).

Sample collection

Soil samples were collected at the end of October 2009. In each park 10 nestling and 10 control sites were chosen at random. At each site the surface of about 100 × 100 cm was marked off, followed by removing dead leaves and plants. Soil samples were collected at the depth of 20 cm from the surface. From each site three samples were collected, put into plastic bags and thoroughly mixed up. Altogether, 40 samples were collected.

Faecal samples, including fresh dropping samples, were taken from four sites in each colony of *Corvus frugilegus* during April 10–30, 2009. The bird faeces were collected into plastic boxes from the sites located under the rook nests.

Sample preparation and analysis

The soil and faecal samples were air dried in the clean laboratory. The soil samples were sieved through a sieve of 2 mm mesh size and 1 g samples were mineralized in mixture of HNO_3 (68 %) and H_2O_2 (30 %) in a microwave mineralizer concentrated nitric acid enriched in oxide hydrogen (3 : 2 cm^3). After mineralization the samples were transferred quantitatively to 25 cm^3 flasks and topped up with distilled water. Faecal samples were dried to constant mass at a temperature 60 ^oC. The samples were homogenized in an agate mortar. Subsamples of 0.5 g weight were mineralized alike the soil samples. The contents of iron, copper, zinc, lead, cadmium in soil and faeces samples were marked with the use of AAS technique (an apparatus manufactured by Carl Zeiss Jena), using acetylene-air flame for analysis: Fe, Cu, Zn, Pb. The content of Cd in samples was determined by means of a graphite cell used as an excitation source. Standard solutions within concentration ranges [$\mu g \cdot cm^{-3}$]: Fe: 50–300, Cu: 0.005–0.100, Zn: 0.5–10.0, Pb: 0.2–4.0 and Cd: 0.001–0.100 were used for the determination of individual metals. In cases of high metals content in the samples, exceeding the concentration range of standard solutions, the examined samples were diluted. Each analysis was repeated twice. Simultaneously, the analyses for the blank test were carried out [21].

On the basis of the results achieved, the mean values of studied parameters for both control points and contaminated sites were calculated. The normal distribution was checked with the use of Shapiro-Wilk's test. Differences between the mean content of individual metals in control points and at contaminated sites were tested with the use of Student's t-test. The content of metals in the rook faeces collected in the two towns was analysed with χ^2 test. All the calculations were done with the use of "Statistica, ver. 10.0."

Results

Out of the five metals examined: Fe, Cu, Zn, Cd and Pb, iron was found in the rook faeces in the highest concentrations (over 1000 $mg \cdot kg^{-1}$) while Cu and Cd concentrations were the lowest (below 1 $mg \cdot kg^{-1}$). The average iron content in the rook faeces collected in Biala Podlaska was 1149.5 ± 208.9 mg · kg^{-1}, which was over twice lower than in Siedlce. (2659.3 ± 479.2 mg · kg^{-1}) (χ^2 = 7941.0 df = 3, $p < 0.001$). Mean values of lead in faeces measured for Siedlce (6.9 ± 2.15 mg/kg^{-1}) did not differ from those measured for Biala Podlaska (7.4 ± 1.70 mg/kg^{-1}, χ^2 = 2.39, df = 3, p = 0.496). However, the content of cadmium in rook faeces from Siedlce (0.94 ± 0.224 mg · kg^{-1}) was four times higher than in Biala Podlaska samples (0.26 ± 0.104 mg · kg^{-1}, χ^2 = 7.47, df = 3, p = 0.058). Also zinc content in rook faeces from Siedlce (41.05 ± 5.07 mg · kg^{-1}) was significantly higher than in the samples collected in Biala Podlaska (30.92 ± 2.69 mg · kg^{-1}, χ^2 = 14.12, df = 3, p = 0.003). However, copper content in the rook faeces collected in both towns was not statistically significant (χ^2 = 0.22, df = 3, p = 0.974) and it was estimated at 0.735 ± 0.128 mg · kg^{-1} in Biala Podlaska and 0.581 ± 0.062 mg · kg^{-1} in Siedlce.

In both towns the concentrations of Fe, Cu, Zn, Pb and Cd were higher at nestling sites than at controls, but in Siedlce the differences for Fe, Cu, Zn and Cd between the two sites were even more apparent (Table 1).

Table 1

Mean values of studied parameters in soils and the calculated values of Student's t-test

Metal	Location	Site	Mean ± SD [mg · kg^{-1}]	Min-max [mg · kg^{-1}]	t	p
Fe	BP	n	3347.5 ± 1310.0	1688.3–5978.0	0.15	0.884
		c	3281.2 ± 541.2	2453.7–4523.0		
	S	n	5013.8 ± 1422.0	2917.3–7299.4	**2.80**	**0.012**
		c	3350.3 ± 1224.3	1526.0–5198.4		
Cu	BP	n	0.477 ± 0.227	0.210–0.990	1.54	0.140
		c	0.365 ± 0.057	0.280–0.450		
	S	n	0.526 ± 0.158	0.340–0.892	**3.63**	**0.002**
		c	0.289 ± 0.135	0.136–0.631		
Zn	BP	n	68.12 ± 56.35	10.66–238.7	0.40	0.690
		c	37.85 ± 11.90	17.76–54.47		
	S	n	60.51 ± 24.32	34.80–110.7	**2.47**	**0.024**
		c	39.37 ± 21.62	15.63–93.36		
Pb	BP	n	23.85 ± 21.88	6.42–75.65	0.37	0.716
		c	21.11 ± 8.42	11.92–40.30		
	S	n	15.63 ± 4.95	8.59–23.34	0.33	0.745
		c	14.92 ± 4.64	9.57–24.61		
Cd	BP	n	0.12 ± 0.10	0.020–0.410	1.60	0.127
		c	0.07 ± 0.04	0.010–0.180		
	S	n	0.20 ± 0.16	0.014–0.461	**2.81**	**0.012**
		c	0.05 ± 0.04	0.006–0.127		

* BP – Biala Podlaska, S – Siedlce, n – nestling sites, c – control sites.

Discussion

Environmental research indicates that birds, on the one hand, contribute to the changes of soil properties caused by deposited faeces [4, 12, 14, 20], and, on the other hand, they are used as bioindicators of environmental contamination by heavy metals [1, 2, 4, 7, 8, 11, 12, 15]. Depending on the type of food consumed and its sources, birds contribute to soil contamination with certain elements. This holds particularly true for colonial birds such as the rook, which was indicated in the present study.

In both towns metal concentrations in the soil were higher at the nestling sites than at the controls. Statistically significant differences in metals content (Fe, Cu, Zn and Cd) between the nestling sites and the controls were observed in Siedlce. Also Fe, Zn and Cd concentrations in the rook faeces in Siedlce were higher than those in Biala Podlaska. Elevated levels of metals in rook faeces sampled in Siedlce, as opposed to those from Biala Podlaska, may indicate higher concentrations of these elements in the former environment, in which the birds fed. Numerous reports point out the fact that birds are sensitive to variation in food available [22–24]. The species under discussion employs a gregarious feeding strategy based on probing the ground [16, 25]. Greater metal values in the rook faeces in Siedlce and a strong influence of the colony of *Corvus frugilegus* roosting in Siedlce upon elevated levels of iron, copper, zinc and cadmium may indicate that environmental levels of these metals are higher around Siedlce than around Biala Podlaska.

During the past years researches on metals concentrations in soil samples taken at random points throughout Siedlce and Biala Podlaska have shown similar lead concentrations in both towns, estimated at 22.6 $mg \cdot kg^{-1}$ [26] and 23.9 $mg \cdot kg^{-1}$ [27] respectively, almost twice greater values of soil iron in Siedlce (2817.0 $mg \cdot kg^{-1}$) than in Biala Podlaska (1501.7 $mg \cdot kg^{-1}$), also two times higher concentrations of Cd (0.31 $mg \cdot kg^{-1}$) and Cu (6.87 $mg \cdot kg^{-1}$) in Siedlce [26] than in Biala Podlaska (0.15 $mgCd \cdot kg^{-1}$ and 3.70 $mgCu \cdot kg^{-1}$) [28]. In Siedlce zinc was present in soil at a higher concentration estimated at 43.2 $mg \cdot kg^{-1}$ than in Biala Podlaska (30.1 $mg \cdot kg^{-1}$). Increased Cd and Zn concentrations in soil in Siedlce, as opposed to Biala Podlaska, may be the result of the local emission of these metals from the galvanizing plant in the former. This was pointed out in the study by Krolak et al [28], in which the dust monitoring results for Siedlce were reported.

The results seem to prove the usefulness of rook faeces as an indicator of metal levels in the environment in which birds feed.

Metals content in bird faeces is determined by a number of factors including the type of bird food, the behaviour and physiological features of birds as well as environmental quality [12, 15]. Metals concentration values in rook faeces sampled in Siedlce and in Biala Podlaska either fell within the range reported for other bird species or were lower (Table 2). The levels of Cd and Pb content in rook faeces in the research area roughly corresponded with those estimated by Spahn and Sherry [13] in the faeces of the blue heron chicks (*Egretta caerulea*) in south Louisiana wetlands.

What is interesting, exactly the same range of Pb content as measured by the authors was estimated by Yin et al [15] in the faeces of the Red-footed Booby (*Sula sula*).

However, considerably higher Zn concentrations, compared to rook faeces, were estimated in the faeces of the Red-footed Booby (*Sula sula*) by Yin et al [15], Caspian Gull (*Larus cachinnans*) by Otero [12], Great Tit (*Parus major*) and Blue Tit (*Parus caeruleus*) by Dauwe et al [3] (Table 2).

Table 2

Heavy metals in faeces of birds according to literature data

Species of birds	Metal [mg $\cdot$ kg^{-1}]					References
	Cu	Fe	Zn	Pb	Cd	
Parus major and *Parus caeruleus*	36.16		400.4–429.4	2.34 –80.4	5.72–16.8	[3]
Rissa tridactyla and *Larus hyperboreus*	5.7–65.0	716–517	63–261	17–32		[11]
Larus cachinnans	30.4–73.9		165.9–397.9	22.9–55.1	2.1–7.7	[12]
Egretta caerulea				1.45–1.59	0.11–0.34	[13]
Sula sula	21.1		419.4		6.34	[14]
	20.0		450	4.26–9.48		[15]
Corvus frugilegus	0.49–0.87	877–3041	27.8–47.0	4.26–9.48	0.14–1.22	Present paper

Contrary to the reports of Orlowski et al. [9, 10], our research shows no evidence that the rook roosting near Siedlce is exposed to excessive Cd and Pb. Based on Cd and Pb estimates in the rook tissues (liver, kidney, lung, bones and muscles), ranging from 17.0–17.2 mgCd $\cdot$ kg^{-1} and 5.0–6.2 mgPb $\cdot$ kg^{-1}, the Authors drew conclusions about acute cadmium contamination and an elevated level of lead in the environment. They reported particularly high levels of Cd, the concentrations of which in all examined tissues were almost identical and ranged between 17.0 and 17.2 mg $\cdot$ kg^{-1} d.m. Our findings show that soil cadmium levels near Siedlce and Biala Podlaska are at least 100 times (or by two orders of magnitude) lower than lead levels. According to Orlowski et al [9, 10], however, Cd concentration in rook tissues was about three times as high as Pb level. The level of cadmium in the tissues of the rook from Siedlce, as estimated by Orlowski et al [9, 10], is surprisingly high. When analyzing the data reported by Orlowski et al [9, 10], we were puzzled at the sample weights (liver, kidney, lung, bones and muscles) ranging between 5 and 151 mg. Sample weights as low as several milligrams are too small to permit accurate determination of trace amounts of cadmium. The cadmium estimates obtained by the Authors might therefore result from the fact that the metal was contained in the reagents used for analysis (so-called blind test).

According to Market [29], a bioindicator is an organism that contains information on the quality of the environment. The rook is particularly sensitive to local environmental contamination by heavy metals taken up with food. Therefore this species can be a good bioindicator of the quality of the environment.

Conclusions

The presence of the rook nestling sites influences the increase of heavy metals content (Zn, Cd, Cu and Fe) in soil.

The content of heavy metals in soil at nestling sites reflects the chemical composition of the rook faeces.

Heavy metals concentration in the rook faeces is determined by the metals content in the environment in which the rook feeds.

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WPŁYW KOLONII LĘGOWYCH GAWRONA NA ZAWARTOŚĆ METALI CIĘŻKICH W GLEBIE

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Abstrakt: Analizowano zawartość metali Cu, Fe, Zn, Cd i Pb w odchodach gawrona bytującego w dwóch koloniach zlokalizowanych w parkach miejskich na terenie wschodniej Polski (Siedlce i Biała Podlaska) oraz wpływ kolonii na zawartość tych metali w glebach. Analizy wpływu kolonii gawrona na zmiany właściwości gleb dokonano, porównując skład chemiczny gleb na stanowiskach pod gniazdami ptaków i na stanowiskach kontrolnych. Odnotowano statystycznie większą zawartość Fe, Zn i Cd w odchodach ptaków gniazdujących na terenie Siedlce niż w Białej Podlaskiej. Istotny, na zawartość Cu, Fe, Zn, Cd i Pb w glebie, okazał się wpływ siedleckiej kolonii gawronów. Nie wykazano wpływu kolonii gawrona na zmiany zawartości Pb w glebie. Skład chemiczny odchodów jest odzwierciedleniem jakości diety ptaków. Przeprowadzone badania wykazały, że gawron jest gatunkiem szczególnie wrażliwym na lokalne zmiany zawartości metali w środowisku.

Słowa kluczowe: gawron, kolonia lęgowa, odchody, gleba, metale ciężkie, zanieczyszczenie, bioindykacja

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EFFECT OF SOIL POLLUTION WITH HEAVY METAL MIXTURES ON IRON CONTENT IN BROAD BEAN (*Vicia faba* L.)

WPŁYW SKAŻENIA GLEBY MIESZANINAMI METALI CIĘŻKICH NA ZAWARTOŚĆ ŻELAZA W BOBIE (*Vicia faba* L.)

Abstract: The investigations were conducted to determine the effect of soil contamination with mixtures of: lead, copper and cadmium with zinc and nickel on two levels of pollution (acc. to II and III pollution class in IUNG classification) on iron concentrations in broad bean plants. Broad bean, White Windsor c.v. was cultivated in a control soil with natural heavy metal concentrations (Control and Control + NPK) and in the soil contaminated with the mixtures of heavy metals (Ni + Zn, Ni + Cd, Ni + Pb, Ni + Cu, Zn + Cd, Zn + Pb, Zn + Cu) applied in two doses, or with single heavy metals (Cd, Cu, Ni, Zn and Pb) used in a higher dose.

Soil contamination with mixtures of Cu and Pb with Zn or Ni and Zn with Ni on the level matching III pollution level in IUNG classification, as well as pollution with mixtures of Cu with Ni and Pb with Zn on the level corresponding to II level of pollution leads to a significant increase in iron concentrations in broad bean shoots but causes its decrease in roots. A decline in Fe content in broad bean roots was observed also under conditions of soil contaminated with mixtures of Ni with Zn, Ni with Pb and Zn with Cu on a lower level of pollution. Cd presence in the mixtures with Ni or Zn, both in a higher and lower dose of the metals leads to alleviating the differences in Fe concentrations in broad bean shoots (and with the lower dose also in roots) in comparison with the control plants.

Keywords: heavy metals, broad bean, accumulation, Fe

Introduction

One of the mechanisms of unfavourable heavy metal effect on plants are disorders in the uptake, transport and assimilation of macro- and microelements. The influence of heavy metals on the uptake and translocation of other cations and anions results from the competition for the sorption site on the root surface or forming unavailable

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complexes. Therefore, heavy metals may lead to secondary deficiencies of other elements, *eg* iron [1–3]. On the other hand, presence of bioavailable iron in soil may also modify heavy metal uptake by plants. Research on iron effect on cadmium absorption by tomato (*Lycopersicon esculentum* Mill.) and morel (*Solanum nigrum* L.) plants or red beet leaves (*Beta vulgaris* var. cicla L.) in hydroponic culture was conducted by Bao et al [4]. Plants suffering from Fe deficiency revealed higher bioconcentration factor and translocation factor towards Cd than plants well supplied with iron. Heavy metals jointly present in soil often show a different effect upon plant than when occurring singly [5]. Because out of the five heavy metals (Pb, Cd, Cu, Zn and Ni) analysed so far and applied separately, zinc and nickel revealed the strongest (negative) effect on broad bean plants growth and also caused considerable changes in macroelement concentrations in plants, including iron, it seemed purposeful to test the effect of soil contamination with mixtures of the above mentioned metals.

The aim of the work was to determine the effect of soil pollution with mixtures of lead, cadmium and copper with zinc and nickel on two levels of pollution (acc. to II and III pollution class in IUNG classification) on growth of broad bean plants and iron concentrations in shoots and roots.

Materials and methods

The experiment was conducted in 2008 on degraded chernozem developed from loess with acid reaction and organic carbon content 1.13 %. Broad bean, White Windsor c.v. was cultivated in a control soil with natural heavy metal concentrations (Control and Control + NPK) and in the soil contaminated with the mixtures of heavy metals (Ni + Zn, Ni + Cd, Ni + Pb, Ni + Cu, Zn + Cd, Zn + Pb, Zn + Cu) applied in two doses (marked respectively “II” and “III” corresponding to II and III class of pollution acc. to the classification suggested by IUNG [6]), or with single heavy metals (Cd, Cu, Ni, Zn and Pb) used in a higher dose (“III”). With regard to the Regulation of the Minister of the Environment dated 9 September 2002 (item 1359), the contents of heavy metals in the initial soil does not exceed the admissible values of concentrations in the soil or ground. After applying heavy metals their concentrations in the soil exceed the admissible values in the case of Zn, Pb (lower and higher dose), Cd and Ni (higher dose). The metal mixtures were used for the soil contamination in the same year when the plants were sampled for analysis, whereas in case of single metals the soil which was contaminated in the year preceding the experiment, *ie* in 2007 was used (it was marked respectively “(1)”). Broad bean was also cultivated in this soil in 2007. Detailed data concerning the level of applied heavy metal doses, the way in which they were supplied to the soil and applied fertilization were presented in previous paper [7]. The samples for chemical analyses were collected at the seed milk maturity. Plant material was washed in tap and in distilled water, dried in 105 ^{o}C to a constant weight and ground to fine powder, then mineralized and dissolved in 10 % HNO_3. After filtration Fe content was measured using Flame Atomic Absorption Spectrometry (FAAS) [8, 9]. The quality of the analytical procedure was controlled by using samples of the reference material in each series of analysis (Certified Reference material CTA-OTL-1 Oriental

Tobacco Leaves). Assessed were also selected parameters of plant growth at that time. The data were processed using software Statistica to compute significant statistical differences between samples ($p < 0.05$) according to Tukey's multiple range test.

Results and discussion

The soil reaction (in KCl) in individual objects after the experiment completion ranged from 4.47 (in ZnIII + NiIII object) to 4.81 (in NiIII + PbIII and ZnIII + CuIII treatment). All tested heavy metal mixtures led to a significant limiting of plant growth, which manifested itself by a shortening of shoot length (Fig. 1). Particularly strong negative effect was observed for mixtures of the examined metals with zinc applied in a dose according to III class of pollution acc. to IUNG classification. Much shorter than control were also broad bean plants cultivated in the soil contaminated with zinc or nickel used separately. On the other hand, cadmium in a mixture with nickel applied in a higher dose contributed to an improved plant growth. Among heavy metal mixtures in a dose established according to II class of pollution, nickel mixtures with copper and zinc mixtures with lead weakened plant growth most. Applied heavy metals did not cause any significant differences in the number of shoots with reference to the control (Fig. 2). Weakening of broad bean growth under conditions of soils contaminated with heavy metal mixtures with zinc in a higher dose and soils contaminated with zinc or nickel used separately, resulted in non-formation of pods by these plants (Fig. 3). Also a

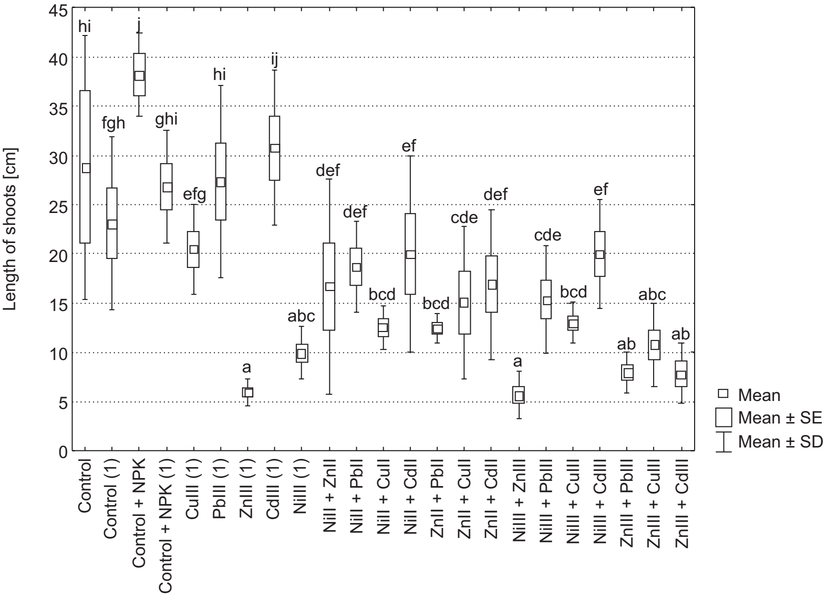

Fig. 1. Length of shoots [cm] of broad bean (*Vicia faba* L.) cultivated in unpolluted soil (Control, Control + NPK) and in soil contaminated with heavy metals. The (1) means the soil, which was polluted and used in year 2007. Values marked with different letters are statistically different at $p < 0.05$

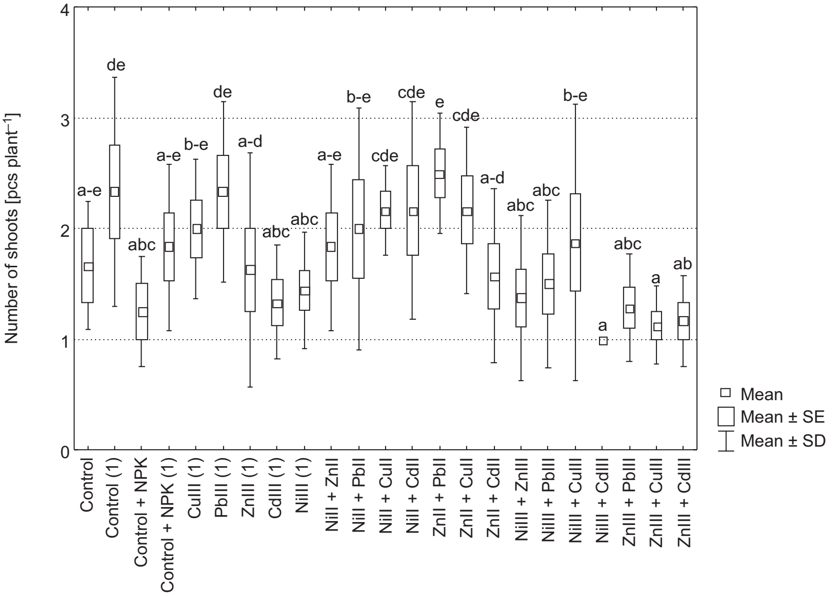

Fig. 2. Number of shoots per plant of broad bean (*Vicia faba* L.) cultivated in unpolluted soil (Control, Control + NPK) and in soil contaminated with heavy metals. The (1) means the soil, which was polluted and used in year 2007. Values marked with different letters are statistically different at $p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

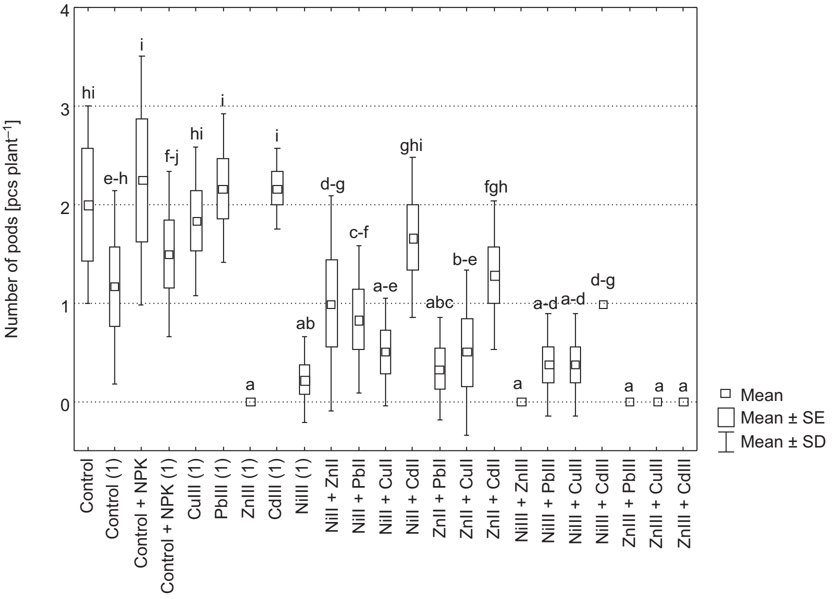

Fig. 3. Number of pods per plant of broad bean (*Vicia faba* L.) cultivated in unpolluted soil (Control, Control + NPK) and in soil contaminated with heavy metals. The (1) means the soil, which was polluted and used in year 2007. Values marked with different letters are statistically different at $p < 0.05$

majority of other tested metal mixtures limited the number of formed pods. There are many examples of adverse effect of heavy metal pollution on growth and yield of plants. The effect depends on the level of contamination, soil type and species of plant [10–12].

Iron level in the legumes ranges quite widely (75–400 mg · kg^{-1} d.m.) [2]. In the analyzed broad bean shoots iron level fell within the 73–318 mg · kg^{-1} d.m. range. Among the analyzed objects, where the soil was contaminated with lower doses of heavy metal mixtures, a significant increase in iron content was registered in broad bean shoots for mixtures of nickel with copper and zinc with lead (Fig. 4). However, soil contamination with heavy metal mixtures in higher doses caused a marked increase in Fe concentrations in all analyzed combinations. The highest level of this element was noted when the soil was contaminated by a mixture of zinc with nickel, zinc with lead or zinc with copper, whereas iron level changed the least when nickel and zinc were

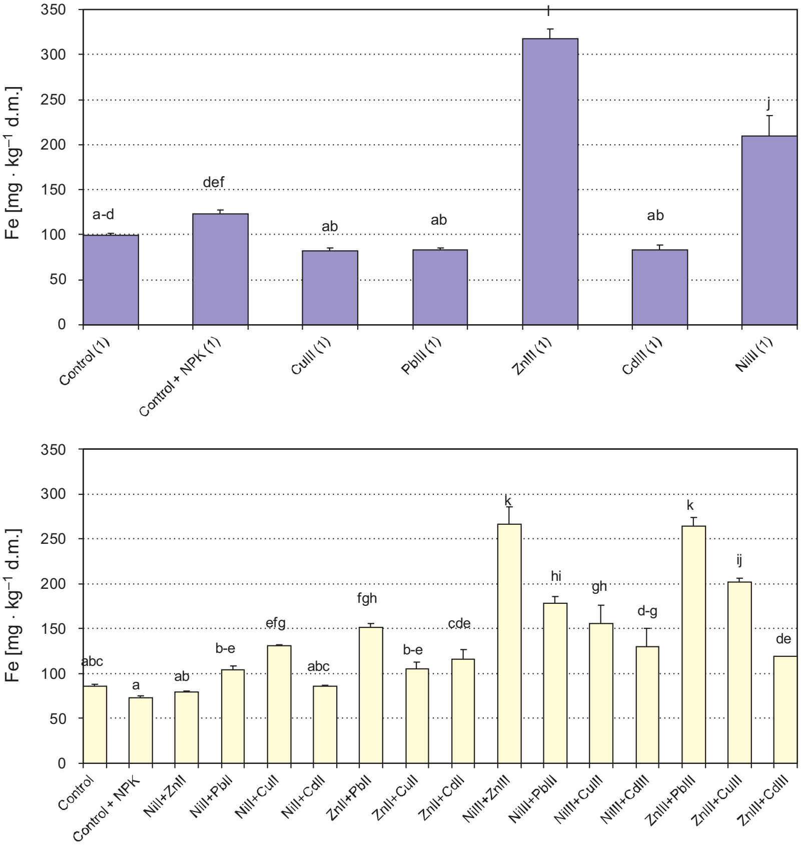

Fig. 4. Iron content in shoots of broad bean (*Vicia faba* L.) cultivated in unpolluted soil (Control, Control + NPK) and in soil contaminated with heavy metals. The (1) means the soil, which was polluted and used in year 2007. Values marked with different letters are statistically different at $p <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

accompanied by cadmium. In case when the soil was contaminated with single heavy metals, the highest iron concentrations were assessed in plant shoots growing in the soil contaminated with zinc (over thrice higher than in the control) and nickel (over twice higher). On the other hand, soil contamination with lead, copper and cadmium did not lead to any significant differences in Fe content in broad bean shoots. A similar tendency was confirmed also in the Authors' previous research [13]. In their research on the response of various soybean cultivars to elevated cadmium concentrations in the substratum (0.00, 0.05 and 0.30 ppm), Smith et al [14] registered a decrease in iron concentrations in plant shoots at the highest cadmium dose (respectively by 14–55 % depending on the cultivar). Also increasing doses of Pb (0, 75, 150, 300 mg · dm^{-3} led to decrease of Fe concentration in shoots of *Solanum melongena* [11], but in this case authors pointed that the treatment provided typical values for this plant grown in alkaline soils, while in our experiment soil revealed acid reaction.

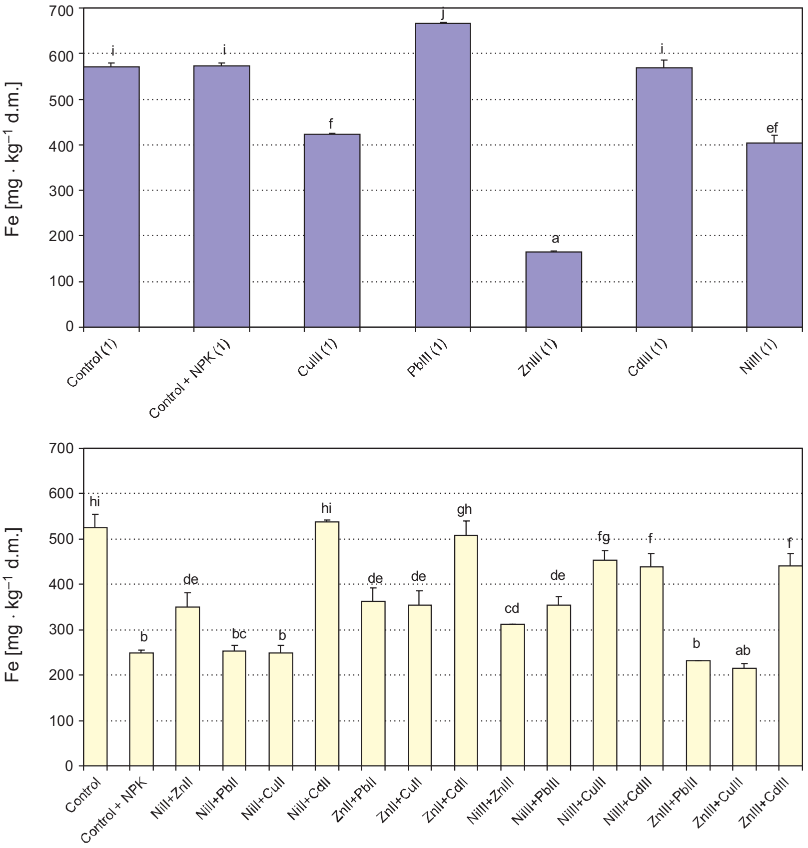

Fig. 5. Iron content in roots of broad bean (*Vicia faba* L.) cultivated in unpolluted soil (Control, Control + NPK) and in soil contaminated with heavy metals. The (1) means the soil, which was polluted and used in year 2007. Values marked with different letters are statistically different at $p < 0.05$

However, iron content looked different in broad bean roots (Fig. 5). Low iron concentration in broad bean roots cultivated in the control soil receiving mineral fertilizers in the year of the experiment was apparent. It was almost twice lower than in control object. According to most authors, the result of mineral fertilization include increased concentrations of soluble iron forms in soil, especially N fertilization [15], although in the research of Santin at al [16] on the effect of increasing P rates, combined with N and K rates on *Ilex paraguariensis* growth and its mineral composition, at higher P rates (400 and 600 mg $\cdot$ dm^{-3} of P_2O_5) iron deficiency symptoms appeared. In our investigation N dose was low due to the broad beans requirement for this macroelement, which may partly explain obtained results. Among the objects with the soil contaminated with heavy metal mixtures the highest concentrations of iron in roots were registered in the objects where the soil was contaminated with a lower dose of zinc with cadmium and nickel with cadmium mixture, and the assessed content was similar as in the control untreated plants, whereas in the other treatments with soil contaminated by the mixtures iron level was the same as assessed in plants receiving mineral fertilizers, or was slightly higher. Among the objects contaminated with single metals, unlike in the case of shoots, broad bean roots growing in zinc polluted soil contained the least amounts of iron (c.a. four times smaller than in the control plants). Also in former research *ca* five times lower iron content was registered in broad bean roots grown in zinc polluted soil [13]. It might have been partially caused by high sulphur content in soil, because zinc was supplied as $ZnSO_4 \cdot 7H_2O$ or resulted from the accompanying decrease in the soil pH. On one hand it is reported that sulphur acts antagonistically on iron metabolism in plants [17], on the other an increase in soil acidification level improves iron bioavailability to plants [2]. Plants developed a number of complicated mechanisms for controlling the acquisition, partitioning and deposition of the micronutrients and ensuring a proper level of individual nutrients. Differences in this respect may refer not only to individual plant species but even to specific specimens and plant parts [18]. Fertilization using swine liquid manure contributed to lowering the soil pH and caused an increase in the exchangeable fractions of such metals as Cd, Cu, Mn and Zn, however did not have such effect for iron or lead. The measure lead to increased content of majority of heavy metals in broad bean leaves but a decline in their content, including iron, in seeds [19]. Fe level in broad bean roots cultivated in the soil polluted with copper and nickel was also lower than in the control plants, whereas in plants from the treatments contaminated with lead or cadmium the level was similar as in the control plants. Cadmium and lead present in the medium variously affected the activity of ferric reductase (FC-R) enzyme in sugar beet roots. This enzyme activity increases at iron deficiency. The reaction depended on the metal dose, its form (chloride salts or chelated with EDTA), iron presence in the medium and exposure time [20]. Cadmium dosed 50 μM $CdCl_2$ or Cd-EDTA, did not affect significantly the activity of the enzyme as such during a two-hour exposure, whereas lead in 2 mM concentration slightly reduced its activity. Short-term exposure (30–60 min) to cadmium and lead of plants previously inducted with FC-R activity through iron deficiency in the medium caused a marked decline in the analyzed enzyme activity. For cadmium the effect was stronger when it was in ionic form than in Cd-EDTA chelate form.

Conclusions

1. Soil contamination with Cu, Pb, Ni and Cd in a mixture with Zn in a dose established on the III level in IUNG classification, and by zinc or nickel only in the same dose leads to a strong weakening of broad bean growth.

2. Soil contamination with mixtures of Cu and Pb with Zn or Ni and Zn with Ni on the level matching III pollution level in IUNG classification, as well as pollution with mixtures of Cu with Ni and Pb with Zn on the level corresponding to II level of pollution leads to a significant increase in iron concentrations in broad bean shoots but causes its decrease in roots. A decline in Fe content in broad bean roots was observed also under conditions of soil contaminated with mixtures of Ni with Zn, Ni with Pb and Zn with Cu on a lower level of pollution.

3. Cd presence in the mixtures with Ni or Zn, both in a higher and lower dose of the metals leads to alleviating the differences in Fe concentrations in broad bean shoots (and with the lower dose also in roots) in comparison with the control plants.

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WPŁYW SKAŻENIA GLEBY MIESZANINAMI METALI CIĘŻKICH NA ZAWARTOŚĆ ŻELAZA W BOBIE (*Vicia faba* L.)

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Abstrakt: Celem pracy było określenie wpływu skażenia gleby mieszaninami metali ciężkich: ołowiu, miedzi i kadmu z cynkiem i niklem na dwóch poziomach zanieczyszczenia (wg II i III klasy zanieczyszczenia zgodnie z klasyfikacją IUNG) na zawartość żelaza w roślinach bobu. Bób odmiany Windsor Biały był uprawiany w glebie o naturalnej zawartości metali ciężkich (Kontrola i Kontrola + NPK) oraz w glebie skażonej mieszaninami metali ciężkich (Ni + Zn, Ni + Cd, Ni + Pb, Ni + Cu, Zn + Cd, Zn + Pb, Zn + Cu) zastosowanymi w dwóch dawkach lub pojedynczymi metalami ciężkimi (Cd, Cu, Ni, Zn i Pb) zastosowanymi w wyższej dawce.

Skażenie gleby mieszaninami Cu i Pb z Zn lub z Ni oraz Zn z Ni na poziomie odpowiadającym III stopniowi zanieczyszczenia wg klasyfikacji IUNG, a także Cu z Ni i Pb z Zn na poziomie odpowiadającym II stopniowi zanieczyszczenia prowadzi do istotnego wzrostu zawartości żelaza w pędach bobu, natomiast powoduje obniżenie jego poziomu w korzeniach. Spadek zawartości Fe w korzeniach bobu stwierdzono także w warunkach gleby skażonej mieszaninami Ni z Zn, Ni z Pb i Zn z Cu na niższym poziomie zanieczyszczenia. Obecność Cd w mieszaninach z Ni lub z Zn, zarówno przy wyższej, jak i niższej dawce metali prowadzi do zniwelowania różnic w zawartości Fe w pędach bobu (a przy niższej dawce także w korzeniach) w porównaniu do roślin kontrolnych.

Słowa kluczowe: metale ciężkie, bób, akumulacja, Fe

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THE IMPACT OF MORPHOREGULATOR ON THE PRODUCTIVITY OF COMMON OATS (*Avena sativa* L.)

WPŁYW REGULATORA WZROSTU NA PRODUKTYWNOŚĆ OWSA ZWYCZAJNEGO (*Avena sativa* L.)

Abstract: The aim of the studies was to consider the use of one registered morphoregulator in the Slovak oats with practical recommendations for the selected (most commonly grown) varieties. Since plant producers are not very experienced in the application of the morphoregulator to some varieties, the most widely grown oat varieties were used in the experiment. The field trial was established in 2009, 2010 and 2011 at the CVRV – VURV (Research Institute for Plant Production) Piešťany, the VŠS (Research Breeding Station) Vígľaš-Pstruša. The impact of the morphoregulator on reducing the stem and enhancing the number of productive tillers was confirmed in all the monitored varieties. Basing on the results of the trial, we do not recommend the application of CCC for 'Auron', 'Atego' and especially 'Valentin' varieties. For 'Vendelin' and 'Zvolen' varieties we recommend to consider the economic acceptability of morphoregulator applications. As economically acceptable we can recommend application of the morphoregulator only for the 'Flamingstern' variety.

Keywords: morphoregulator, lodging rate, oat (*Avena sativa* L.), stem, tillers

Introduction

Synthetic regulators of plant growth are classified as phytohormone analogues and growth retardants depending on their chemical structure and physiological effects on plants [1].

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Tolbert [2, 3] was the first who described the effect of the morphoregulator chlormequat chloride [CCC, chlormequat (2-chloroethyl)-trimethylammonium chloride] on growth and shoot elongation in wheat. Applications of chlormequat to field plots of cereals at the 3- to 5-leaf growth stages reduced the height of wheat (*Triticum aestivum* L.) the most, followed by barley (*Hordeum vulgare* L.), and oats (*Avena sativa* L.). Height reductions were cultivar-specific in the three crops. Lodging was temporarily delayed by the use of chlormequat, while disease incidence, seed yields, protein, lignin, and cellulose content of the straw were unchanged. Of 53 barley cultivars treated with chlormequat, 35 showed variable degrees of height reduction with 5 reduced significantly to a maximum of 13.2 %; 6 showed no response, while 12 grew taller following treatment. In general, the reaction of barley cultivars to chlormequat followed the genetic relationships similar to those determined by isozyme patterns [4].

The influence of growth regulators chlormequat chloride, ethephon, trinexapac-ethyl, and a combination of chlormequat chloride and ethephon on decreasing sunflower height was examined in the years 2006–2009. Height was reduced by as much as 63 cm by double application of chlormequat chloride (915 g $\cdot$ ha^{-1}) + ethephon (465 g $\cdot$ ha^{-1}) at early and later growth stages (BBCH 32 and 50) [5].

The major factor associated with lodging sensitivity is the length of the stem. Lodging is often associated with quantity and quality losses in grain yields and evidently increases harvesting and drying expenses. Abundant nitrogen fertilization, in combination with high precipitation, favours stem elongation and hence results in increased risk of lodging. At high latitudes the long days and a low angle of incident radiation further promote stem elongation. Inhibiting stem elongation by PGR application generally reduces the risk of lodging. To shorten the stem, PGRs are applied at early stem elongation phases (CCC) [6].

CCC and ethephon applied to oat prior to onset of stem elongation resulted in similar short-term reduction in stem elongation of the main shoot and T1 and T2 tillers [7]. This indicates that even when tillers are not directly exposed to PGR application, the elongation retarding effect may be transferred to the tillers [7]. Application of plant growth regulators (PGR) to control lodging in cereal crops often increases the number of tillers and/or spikes. Spring barley plants treated with an early application of CCC (ZGS 13 or ZGS 30) or ethephon (ZGS 30) produced greater numbers of shoots, appearing later in time, than control plants. Early PGR treatment increased the number of spike-bearing shoots, primarily by enhancement of tiller numbers (tiller-derived spikes) rather than the spike production rate (tiller survival) [8].

The highest decrease in plant height of winter wheat was obtained in treatments where for the first time CCC was applied at a rate of 1 dm^3 $\cdot$ ha^{-1} and for the second – Modus 0.4 dm^3 $\cdot$ ha^{-1}, Terpal C 0.7 dm^3 $\cdot$ ha^{-1}, or Cerone 0.5 dm^3 $\cdot$ ha^{-1} at BBCH 39–45 were used [9].

When PGR treatments prevent lodging or reduce its magnitude, the advantageous effects on yield quality and quantity and easier harvesting are likely to make the treatments profitable. When there is no lodging PGR treatments should increase the yield to cover at least the management expenses to be cost-effective. To reach this threshold level, 150 to 300 kg · ha^{-1} yield improvement is likely to be the minimum requirement, depending on the crop and PGR [6].

In Slovakia there are only two preparations registered in non-food oats that contain the active substance chlormequat chloride. These are: Retacel Extra R 68 and Chlormelam 720 SL. The permitted rate is 3.5 dm^3 · ha^{-1} from the appearance of the first node to the second node (BBCH 31–32) [10].

The effects of single and repeated early applications of chlormequat (at up to and including Zadoks growth stage (GS) 32) on the growth and development of the winter oat cultivar 'Bulwark' were investigated in two seasons of field experiments at Tenby, UK. At maturity, reductions in stem length and lodging were best achieved by chlormequat applied at GS 32; this treatment shortened the stems by an average of 24 % in 1985/86 and 31 % in 1986/87. Earlier applications were significantly less effective [11].

Field plot experiments were established for studying the influence of growth regulators MLU 208, MLU 2081 [various mixtures of 2,3-dichloroisobutyric acid (DCiB) with chlormequat chloride (CCC)] and CCC on the length of shoot axis, susceptibility to lodging and grain yield of oats (*Avena sativa* L.) and oil seed rape (*Brassica napus* L.). With the lodging-resistant oat varieties 'Alfred' and 'Solidor', MLU 208 and MLU 208L caused stem reductions of 10 % and yield increases up to 6.5 % despite the fact that the untreated controls showed hardly any lodging. CCC, applied as comparative treatments, had no yield-increasing effect although a stem reduction of approx. 8 % was recorded [12].

Lodging of oats during growth is more frequent than when growing wheat or barley. It coheres with the higher number of sclerenchym cells in the stem in the above mentioned crops and is more traumatic for oat producers.

The aim of the experiments was to consider the use of one registered morphoregulator in the Slovak oats with practical recommendations for the selected (most commonly grown) varieties.

Material and methods

The field experiment was conducted in 2009–2011 at CVRV-VÚRV Piešťany, in the VSS Vígľaš-Pstruša characterised as a potato-wheat production area (altitude 375 m), with an average annual temperature of 7.76 °C and annual precipitation of 611 mm. The oats were sown in a crop rotation always after red clover in four replications on a plot of the size of 10 m^2. Nitrogen fertilizer rates were applied with respect to inorganic nitrogen in the soil.

Phosphorus fertilization (in the form of Amofos 21 % P) 12 kg · ha^{-1} and potassium (as potassium salt 60 % K_2O) 96 kg · ha^{-1} were applied once, in autumn. Nitrogen in the form of ammonium nitrate with dolomite (27 % N) was applied before sowing, for the planned harvest of 4 Mg · ha^{-1}.

The most frequently grown varieties of common oat of Slovakia were the object of investigation in the experiment. From the total of six tested oat varieties, three ('Zvolen', 'Vendelin' and 'Valentin' varieties) were bred at the VŠS Vígľaš-Pstruša, two varieties were of Czech origin ('Auron' and 'Atego') and one of German origin

(‘Flamingstern’ variety). Each variety was planted with the same quantity of germinating grains – 5.0 million per 1 ha.

For each variety there was a variant treated by morphoregulator Retacel Extra R 68 (CCC), at a rate of 3.5 $dm^3 \cdot ha^{-1}$ applied in the phase between the first and second node (BBCH 31–32), and the untreated variant. The block method of sowing was used in the trial with random arrangement of plots. Sowing was performed using the Řyord sowing-machine at the plot “Kostolisko I” on 5th April 2009 for the first time, at the plot “Tri duby” on 1st April 2010 for second time and in the third trial at the plot “Kocaň I” on 28th March 2011. Harvesting was carried out with the Wintersteiger harvester on 3rd August 2009, 9th August 2010 and 10th August 2011. Meteorological characteristics are shown in Table 1.

Table 1

Meteorological characteristics of the experimental plot in 2009–2011

Month	March	April	May	June	July	August
Temperature [°C]						
Average (last 50 years)	2.8	8.4	13.1	16.3	17.8	17.3
2009	3.4	11.5	14.4	16.1	19.8	19.5
2010	2.5	9.1	13.6	17.5	20.6	17.6
2011	4.3	10.8	13.5	17.5	20.5	17.6
Precipitation [mm]						
Average (last 50 years)	29.8	46.7	63.9	85.2	75.6	62.0
2009	49.4	11.0	62.8	96.4	34.2	35.6
2010	52.2	55.0	132.8	207.1	100.2	121.9
2011	8.1	55.0	61.2	85.7	123.2	34.7

The effect of the morphoregulator on the crop structure of each variety was investigated, *ei*: average height, lodging before harvest (according to point breeding scale 1–9), the number of productive tillers on m^2 and yield. On the basis of these results the height reduction, stage of lodging reduction and increase of productive tillers number was calculated.

The results were processed statistically using analysis of variance (ANOVA) followed by testing according to LSD.

Results and discussion

The application of the morphoregulator strongly influenced the structure of the crop (average height, lodging and number of productive tillers) but was also strongly influenced by variety and year (Tables 2 and 3). This fact is confirmed by the Peltonen-Sainio and Rajala [13], who confirmed the CCC treatment had resulted in more panicles per square meter. The results are in agreement with the previous finding of Rajala [6] who observed a reduction in stem elongation, shoot growth and that

Table 2

Modeling of some characteristics of ‘Auron’, ‘Atego’ and ‘Zvolen’ varieties of oats after application of morphoregulator

Specification	Morpho-regulator	‘Auron’			Average	‘Atego’			Average	‘Zvolen’			Average
Year		2009	2010	2011		2009	2010	2011		2009	2010	2011	
Average height [cm]	—	105.0	117.0	103.0	108.3 bB	98.0	110.0	97.0	101.7 bB	100.0	114.0	102.0	105.3 bB
	CCC	102.0	101.0	97.0	100.0 aA	88.0	92.0	92.0	90.7 aA	98.0	99.0	95.0	97.7 aA
$LSD_{0.05}$ test (small letters) $LSD_{0.01}$ test (big letters)					2.93 4.02				3.04 4.18				3.20 4.40
Height reduction [%]		2.3	5.7	5.9	4.6	10.3	16.4	5.2	10.6	2.0	13.2	6.9	7.0
Lodging before harvest (point breeding scale 1–9)	—	7.0	7.0	7.0	7.0 aA	9.0	7.0	8.0	8.0 aA	8.0	7.0	8.0	7.7 aA
	CCC	8.0	7.0	8.0	7.6 aA	9.0	8.0	9.0	8.6 aA	9.0	8.0	9.0	8.66 bB
$LSD_{0.05}$ test (small letters) $LSD_{0.01}$ test (big letters)					0.87 1.22				0.92 1.26				0.53 0.73
Stage of lodging reduction (point breeding scale 1–9)		1.0	0.0	1.0	0.66	0.0	1.0	1.0	0.66	1.0	1.0	1.0	1.0
Number of productive stems on m^2	—	572.0	508.0	488.0	522.7 aA	576.0	548.0	536.0	570.7 aA	548.0	504.0	504.0	518.7 aA
	CCC	640.0	532.0	600.0	590.7 bB	636.0	660.0	588.0	610.7 bB	584.0	516.0	572.0	557.3 bB
$LSD_{0.05}$ test (small letters) $LSD_{0.01}$ test (big letters)					18.40 22.27				13.62 18.71				11.76 16.15
Increase of productive tillers [%]		11.9	10.5	22.9	15.1	10.4	20.4	9.7	10.3	6.5	2.3	13.4	7.4

Table 3

Modeling of some characteristics of ‘Vendelin’, ‘Valentin’ and ‘Flamingstern’ varieties of oats after application of morphoregulator

Specification	Morpho-regulator	‘Vendelin’			Average	‘Valentin’			Average	‘Flamingstern’			Average
Year		2009	2010	2011		2009	2010	2011		2009	2010	2011	
Average height [cm]	—	107.0	112.0	102.0	107.0 bB	91.0	105.0	94.0	96.7 bB	97.0	114.0	97.0	102.7 bB
	CCC	100.0	87.0	98.0	95.0 aA	80.0	95.0	87.0	87.3 aA	89.0	102.0	96.0	95.7 aA
LSD$_{0.05}$ test (small letters) LSD$_{0.01}$ test (big letters)					4.93 6.77				1.44 1.98				2.53 3.48
Height reduction [%]		6.5	23.3	4.0	11.3	12.1	9.5	7.5	9.7	8.8	10.5	1.1	6.8
Lodging before harvest (point breeding scale 1–9)	—	7.0	7.0	7.0	7.0 aA	9.0	8.0	9.0	8.66 aA	6.0	6.0	6.0	6.0 aA
	CCC	8.0	9.0	8.0	8.33 bB	9.0	9.0	9.0	9.0 aA	7.0	7.0	7.0	7.0 bB
LSD$_{0.05}$ test (small letters) LSD$_{0.01}$ test (big letters)					0.82 1.13				0.47 0.64				1.01 1.38
Stage of lodging reduction (point breeding scale 1–9)		1.0	2.0	1.0	1.33	0.0	1.0	0.0	0.33	1.0	1.0	1.0	1.0
Number of productive stems on m^2	—	496.0	536.0	560.0	530.7 aA	568.0	544.0	590.0	567.3 aA	536.0	510.0	495.0	513.7 aA
	CCC	540.0	584.0	660.0	594.7 bB	688.0	592.0	696.0	658.7 bB	624.0	582.0	536.0	580.7 bB
LSD$_{0.05}$ test (small letters) LSD$_{0.01}$ test (big letters)					13.07 17.95				15.97 21.93				10.0 13.73
Increase of productive tillers [%]		8.8	8.9	17.8	11.8	21.1	8.8	17.9	15.9	16.4	14.1	8.3	12.9

Table 4

Average yields after application of morphoregulator (varieties: ‘Auron’, ‘Atego’, ‘Zvolen’, ‘Vendelin’, ‘Valentin’, ‘Flamingstern’)

Variety	Morphoregulator	‘Auron’			‘Atego’			‘Zvolen’		
Year		2009	2010	2011	2009	2010	2011	2009	2010	2011
Yield [Mg · ha^{-1}]	—	6.54	4.76	5.95	6.22	4.47	5.22	6.66	4.82	5.26
	CCC	6.33	4.51	5.75	6.29	4.28	5.14	7.21	4.54	5.18
Average	—	5.76			5.30			5.58		
	CCC	5.53			5.24			5.64		
Variety	Morphoregulator	‘Vendelin’			‘Valentin’			‘Flamingstern’		
Year		2009	2010	2011	2009	2010	2011	2009	2010	2011
Yield [Mg · ha^{-1}]	—	6.61	4.90	5.86	7.55	4.94	5.73	5.91	3.95	4.47
	CCC	6.79	4.71	5.94	7.13	4.61	5.57	6.18	4.58	4.53
Average	—	5.79			6.07			4.78		
	CCC	5.81			5.77			5.10		
LSD total – years	$\alpha \le 0.05$	0.242								
	$\alpha \le 0.01$	0.327								
LSD total – treatment	$\alpha \le 0.05$	0.198								
	$\alpha \le 0.01$	0.267								
LSD total – varieties	$\alpha \le 0.05$	0.342								
	$\alpha \le 0.01$	0.462								

elongation may change assimilate demands and distribution within the plant and thus provide excess resources that in turn may stimulate, for example, root growth, tiller and spikelet initiation and grain set and growth. Tripathi et al [14] detected the most consistent effect of chlormequat and ethephon on reduction in plant height and when environmental conditions are conducive to lodging, these reductions in plant height are often accompanied by reductions in lodging.

All varieties identically responded in all the years by reducing their height – at least by 1.1 % (‘Flamingstern’ variety in 2011) to 23.3 % (‘Vendelin’ variety in 2010). The impact of the morphoregulator on lodging before harvest, expressed on a scale from 1 to 9, was not very marked and especially varieties with a high resistance to lodging (‘Valentin’, ‘Atego’ or ‘Auron’ varieties) were not influenced by CCC in some years. The morphoregulator quite significantly increased the number of productive tillers in all tested varieties and in all the years (the ‘Zvolen’ variety achieved the lowest growth and the ‘Auron’ variety reached the highest, *ie* 2.3 % in 2010 and 22.9 % in 2011, respectively) (Tables 2 and 3).

The results presented in Table 4 refer to the significant influence of the variety on the yields of oat grain and also significant differences between the experimental years, which is in accord with the above mentioned quotations.

The lowest oat yields were obtained in 2010 when the highest total sum of precipitation (especially from May to August) and the lowest temperature in two spring months (March, April) was noted (see Table 1). The negative effect on the yield of all oat varieties was statistically confirmed. No significant differences were detected in the yields of grain treated by the morforegulator and the untreated variant. Browne et al [15] also confirmed not significant effect of chlormequat chloride on the yields of oat.

The yields of ‘Valentin’ and ‘Vendelin’ varieties were statistically significantly higher than of ‘Flamingstern’ and ‘Atego’ varieties. ‘Valentin’, ‘Vendelin’ and ‘Auron’ varieties achieved significantly higher yields than ‘Zvolen’, ‘Atego’ and ‘Flamingstern’ varieties. The yields of ‘Zvolen’ variety were significantly higher than of ‘Flamingstern’ variety. On the whole we can evaluate the impact of morphoregulators as positive, however only a non-significant effect on the increase of yields of the ‘Zvolen’, ‘Vendelin’ and especially ‘Flamingstern’ varieties. This is related mainly to a medium (‘Vendelin’ and ‘Zvolen’ varieties) and lower (‘Flamingstern’ variety) resistance to lodging. On the contrary we can assess the impact of the morphoregulator as negative (yield reduction) but also with non-significant effects on the ‘Auron’ and ‘Atego’ and especially ‘Valentin’ varieties. This is related with a medium (‘Auron’ variety) and high resistance to lodging (‘Atego’ and ‘Valentin’ varieties).

The average price of the product Retacel R 68, according to the prices of the company Alchem, is 4.19 EUR per litre VAT excluded (5.028 EUR per litre VAT included). At a rate of 3.5 litres per ha the cost is 17.598 EUR VAT included.

Conclusions

1. Overall the average yield of oat in three-year field experiments reached 5.53 $Mg \cdot ha^{-1}$.

2. ‘Vendelin’ and ‘Valentin’ oat varieties reached the highest whereas ‘Flamingstern’ variety the lowest average harvests in the trial.
3. The negative effect on oat yielding was statistically confirmed in 2010, when the highest total sum of precipitation during the vegetation season and the lowest temperature in the spring was registered.
4. It was confirmed a significant effect of the variety and insignificant impact of CCC on the dynamics of oat grain yields.
5. In case of all varieties and years the impact of CCC on reducing the tiller height and increasing its productive numbers was confirmed. The effect of CCC on lodging before harvest, expressed on a scale from 1 to 9, was not considerable, especially for ‘Valentin’, ‘Atego’ or ‘Auron’ varieties with a high resistance to lodging.
6. The application of CCC for ‘Auron’, ‘Atego’ and especially ‘Valentin’ varieties is not recommended, for ‘Vendelin’ and ‘Zvolen’ varieties it can be recommended after considering the economic viability, but we can recommend CCC application only for the ‘Flamingstern’ variety.

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WPŁYW REGULATORA WZROSTU NA PRODUKTYWNOŚĆ OWSA ZWYCZAJNEGO (*Avena sativa* L.)

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Abstrakt: Celem badań było rozważenie stosowania jednego z zarejestrowanych regulatora wzrostu w uprawie owsa z praktycznymi zaleceniami dla wybranych, najczęściej uprawianych odmian w Słowacji. Ponieważ producenci nie mają dużego doświadczenia w stosowaniu regulatora wzrostu w uprawie niektórych odmian, w doświadczeniu uwzględniono najpowszechniej uprawiane odmiany owsa.

Doświadczenia polowe zakładano w latach 2009, 2010 i 2011 w CVRV-VURV (Instytut Badawczy Uprawy Roślin) Piešťany, VSS (Stacja Badawcza Hodowli) Vígľaš-Pstruša. Dla wszystkich monitorowanych odmianach został potwierdzony wpływ regulatora wzrostu na skrócenie źdźbeł i zwiększenie liczby pędów produkcyjnych. Na podstawie wyników badań nie zaleca się stosowania CCC w przypadku odmian 'Auron', 'Atego', a zwłaszcza 'Valentin'. W przypadku odmian 'Vendelín' i 'Zwolen' zaleca się rozważenie efektywności ekonomicznej stosowania tego regulatora wzrostu. Tylko w przypadku odmiany 'Flamingstern' można zalecić stosowanie CCC jako ekonomicznie akceptowalne.

Słowa kluczowe: regulator wzrostu, wskaźnik wylegania, owies (*Avena sativa* L.), źdźbło, pędy

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ORGANIC MULCHES IN THE VEGETABLE CULTIVATION (A REVIEW)

MULCZE ORGANICZNE W UPRAWIE WARZYW

Abstract: Soil mulching is very important practice in field production. Different mulching materials can be use for different agricultural and horticultural species in different climatic environments. The main role of organic mulches is to protect the soil surface from the influence on unfavorable factors and to improve the growing conditions for the crop plants. Mulching reduces unproductive evaporation from the soil surface. Organic mulch also reduces soil wind and water erosion by protection the soil surface and reduces nutrient loss by runoff and leaching. Mulches conserve soil moisture, help maintain stable soil temperature, increase soil porosity and suppress weed growth. The main advantages of organic mulches are organic matter and nutrient supply not only for plants but also for soil organism. Mulch improves physical, chemical and biological properties of soil and ultimately enhances the growth and yield of crops. The purpose of this review is to comparative analysis of the scientific research on the benefits and drawbacks of mulches used in vegetable cultivation.

Keywords: mulch, cash crop

Nowadays, care for the environment and ecological issues, is not only a kind of ideology, but it has wide application in practice. It is said about it in the context of the development of the industry, but also in relation to agriculture. In the cultivation of plants it is very important not only yield level, but the least invasive course of all phases of cultivation. Very often are used environment-friendly, natural methods of soil conservation. According to Kołota and Adamczewska-Sowinska [1] all treatments that protect the soil from degradation and use plant protection methods other than chemicals are of great importance in organic farming. One of the natural methods which have a favourable influence on soil environment is the use of mulches [2–4]. To achieve optimum advantage from the mulch, the mulch should be applied immediately after germination of seeds, at a minimal dose of 5 ton per ha [5]. A mulch may take many forms: a living plant ground cover, loose particles of organic and inorganic matter spread over the soil or sheets of artificial or natural materials laid on the soil surface. Plants residues from preceding crops may also be used to form a mulch [6]. Organic

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mulches have the advantage of being biodegradable, but decomposition may result in a temporary reduction in soil mineral nitrogen. According to Bajoriene et al [7] natural organic mulch eventually breaks down and becomes a part of the soil and a source of plant nutrients. Increasing the amount of soil organic matter is regarded as the main advantage of organic mulch. However, the influence of mulch on soil agrochemical properties depends on the chemical composition of mulch. Organic mulch is a source of nutrients for soil microorganisms, and as a result of their activity organic residues used for mulching are decomposed to available plant nutrients [8, 9]. Organic mulches provide many of the benefits but also have few disadvantages. Natural mulch materials are often not available in adequate quantities for commercial operations or must be transported to the place of use. Natural materials are not easily spread on growing crops and require considerable hand labor. Expense and logistical problems have generally restricted use of organic mulch to home gardeners and small market gardens with only limited use on a large commercial scale [5]. In turn, synthetic mulches provide an effective barrier to most weeds and are amenable to mechanized application, but they must be removed at the end of the season. What is more non-porous plastic mulches can hinder infiltration of rainfall or overhead irrigation into the crop root zone. Some water runs into planting holes, but much of it runs off the mulch into alleys and may not reach crop roots. Other disadvantage of synthetic mulches include the labor of end-of-season removal, is generation of non-biodegradable waste, and the fact that synthetic mulches do not add organic matter or nutrients to the soil [10]. According to Zagaroza [11] inconveniences is mainly the price of plastic as well as management costs.

The effect of mulching on the soil properties and plant yield depends on the climatic and soil conditions, agro-technology practices and the kind of mulch. This treatment gives better results in less favourable soil conditions, in areas with a high abundance of weeds and at lower soil nutrients [12]. The main role of mulches in vegetable crops cultivation is to protect the soil surface from the influence of unfavorable factors and to improve the growing conditions for the crop plants [7, 13]. They reduce soil wind and water erosion [14], conserve soil moisture [15] and help maintain stable soil temperature [16]. The properties of some mulches may better benefit plants growth by preserving soil structure and acting as a barrier to the action of rainfall that can cause compaction and erosion. Less-compacted soil provides a better environment for seedling emergence and root growth [17]. Soil coverage with organic mulches is one of the natural methods of preventing weed infestation. Organic mulch can block light to the soil surface, reducing the germination and growth of weeds. Infestation is limited by both the mechanical effect of an application of mulch [18], and by the allopathic effect of chemical compounds contained in the tissue of plant mulches [19]. This allows farmers to reduce an application of herbicides and tillage operations which disturb soil structure [14].

Soil physical and chemical properties

Agricultural production is directly related to quality of soil. Maintenance of proper soil quality is essential not only for agricultural sustainability, but also for environmental protection. Many materials used for mulch have different effects on soil physical and chemical characters. According to Bezborodova et al [20] the potentialities of mulches to improve soil structure, increase organic matter, and establish patterns of nutrient cycling more similar to natural ecosystems. Mulching positively influences the biodiversity and abundance of soil fauna [21].

The presence of mulches on the field during vegetation period reduces the need for some soil tillage operations, which can contribute to soil compaction and dispersion [1]. According to Mulumba and Lal [22] effect of mulching on bulk density are often variable and may vary due to soil type and properties, type of mulch and climate. Pervaiz et al [23] were observed that straw mulch decreased bulk density of the soil. In turn, Bottenberg et al [24] reported increase soil bulk density under mulch. Mulumba and Lal [22] were found that total soil porosity increased with increase in mulch rate by 35–46 %, however bulk density was not affected by mulch rate. The increased porosity is especially important to crop development since it may have a direct effect on soil aeration and can enhance root growth. According to Dexter [25] organic mulch also affect in a high degree on the aggregate stability. The author claim that changes in soil organic matter content can lead to changes in aggregation stability. The energy dissipation effect of organic matter helps to reduce aggregate breakdown by raindrop impact. The increased aggregation due to mulches application can also be attributed to increase in fungal and bacterial activity [22]. Jordan et al [26] reported that bulk density, total soil porosity and aggregate stability could be improved significantly with the increasing mulch rates.

In the study by Lal [27] use of crop residue mulch and no till system was an effective technique to reduce risks of erosion-induced soil degradation. The author also indicated that soil erosion decreased drastically with increasing mulch rate in all no till treatments. Lal [28] claim that the cropping systems should be developed that provide ground cover at all times especially during the periods of intense rains. According to Smets et al [29] organic mulches can be used to quickly protect the soil surface against the erosive forces of rain and runoff. This is confirmed in the study by Gholamia et al [30] in which straw mulch played an effective role in reducing the erosion in both up and down directions.

According to Cherr et al [9] the main advantages of organic mulches are organic matter and nutrient supply not only for plants but also for soil fauna. The soil organic matter increases due to decomposition of applied mulch. The remains of mulch were returned into the soil by ploughing after harvest in the autumn. Blanco-Canqui and Lal [31] were found that mulching with straw during 10 years increased soil organic carbon by 33 %. This means that 2/3 of the applied straw was not converted into SOC and probably was lost as emissions of CO_2 and CH_4. This is confirmed in the study by Yu et al [32], in which soil organic carbon content increased significantly after six years straw application. In the study by Bajoriene et al [7] peat, straw and sawdust mulch had a positive influence on the SOC content increasing it 1.3–1.9 times. The thicker (10 cm) mulch layer significantly (by 0.35–0.52 percentage points) increased the content of SOC compared with the thinner (5 cm) mulch layer. The authors also found a very strong positive linear correlation between the content of organic C carried into the soil with mulch and the content of organic C in the soil.

The conservation of soil water storage through mulching is one of the important purposes. When soil surface is covered with mulch helps to reduce evaporation and increase infiltration of rain water during growing season [5]. Sauer et al [33] reported a 34–50 % reduction in soil water evaporation as a result of crop residues mulching and that creating a 15-cm bare strip increased soil water evaporation by only 7 % over the weathered residue cover. Mulches greatly retard the loss of soil water. As a result, higher and uniform soil water regime is maintained reducing the irrigation frequency [34]. In the study by Kosterna [35] it was found that all investigated in the experiment kinds of straw caused increase moisture the upper and lower soil layers. Tomar et al [36] demonstrated higher soil moisture at the depth of 0–30 cm in mulched plots compared with the control. According to those authors, the effect of mulching was less pronounced at the 30–90 cm depth, but mulches retained relatively more water than the control. Also Rathore et al [37] reported that straw mulch conserved more water in the soil profile during the early growth period compared to no mulch. According to Sinkeviciene et al [16], soil moisture in mulched plots is not only higher compared with control plots but also more stable during all growing periods. Studies by Shangning and Unger [15], as well as by Uwah and Iwo [38], indicated that straw mulching increases soil moisture with an increasing straw dose used for mulching. Similarly, in the study by Jordán et al [26] low mulching rates did not have a significant effect on water properties with respect to control, although the available water capacity increased greatly under high mulching rates. The authors also found that after simulated rainfall experiments the mulch layer contributed to increase the roughness and the interception of raindrops, delaying runoff generation and enhancing the infiltration of rain water during storms. Mulching contributed to a reduction in runoff generation and soil losses compared to bare soil.

Soil mulching with organic material is one way of soil water protection and also helps maintain a constant soil temperature in soil layer within the root system of crops [16, 35, 39]. Kumar and Bhardwaj [5] found that mulch reduces soil warming in summer and cooling in winter. It prevents the extremes of temperatures. The cooling effect of soil in summer promotes root development. According to the authors the effect of mulching on the temperature regime of the soil varies according to the capacity of the mulching material to reflect and transmit solar energy. In general, mulch, by maintaining proper moisture and decreasing soil warming in summer months as well as reducing the daily temperature fluctuations, improves soil conditions for plant growth and development. This was confirmed in studies by Kesik and Maskalaniec [40], in which mulch with rye straw was used effectively as an insulator and protected the soil from overheating. Mulching of soil ensured better thermal conditions during the morning hours, and protected against rapid loss of warmth accumulated in the soil during the day. The soil temperature in the study by Kosterna [39] in the plots without straw, both in the morning (measurement at 8.00 a.m.) and in the afternoon (measurement at 2.00 p.m.) was higher than in plots mulched with straw. According to Borowy [41] this phenomenon can be unfavourable for thermal plants. The covers caused decrease of soil temperature and as a result contributed to slower growth of plants and delayed fruits maturation.

Weed control effect

Soil coverage with organic mulches can suppress weed infestation. According to Ossom et al [42] very little weed growth occurs under the mulch as the mulches prevent penetration of light or exclude certain wavelengths of light that are needed for the weed seedlings to grow. Weber and Hrynczuk [43] (in Klumper et al [44]) were found that germination of some weed species depends on the so-called light reaction which stimulates plant emergence. Cardina et al [45] and Mohler and Teasdale [46] claim that lack of light makes weeds remain dormant in the top soil layer, and as a result, no infestation of crop plants takes place. According to Creamer et al [19] infestation is also limited by the allopathic effect of chemical compounds contained in the tissue of plant mulches. The authors also found that cover crop residues remaining on the soil surface can physically modify seed germination by altering the seed environment (changes in light availability, soil temperature, and soil moisture). A positive effect of various organic mulches is particularly visible in the period of intensive weed germination in the first part of summer [47]. The authors found that in the second part of summer and in early autumn, weed emergence is weaker in comparison with that in spring and early summer, therefore, mulch has less influence. The number of weeds that germinated in the beginning of summer in mulched soil was by 30.9–50.6 times lower than in the soil without mulch. Later this positive influence weakened, but remained for the entire growing period.

In the study by Kosterna [48] all types of mulch caused a decrease in weed infestation in broccoli and tomato compared to the control plot without mulch. The most efficient for limiting infestation was mulch with buckwheat and rye straw. This was confirmed by a study by Jodaugiene et al [47] regarding kidney beans and onion cultivation, in which the most efficient weed limiter at the beginning of summer (3.5–14.1 times) was straw mulch. However, the authors pointed that straw should not to contain weed or crop seeds, which could cause secondary infestation. In turn, Yordanova and Shaban [49] found that straw mulch is more loose material, did not cover the soil tightly and could not provide effective weed control compared with other kinds of organic mulch. In a study by Mohtisham et al [50], mulch with wheat and maize straw reduced the number of germinating weeds by half compared to non-mulched control. Similarly, in the study by Sinkeviciene et al [16] straw mulch was the best for weed control in vegetable cultivation. In plots with straw mulch weed density was established at 2.8–6.4 times lower compared with weed density in plots without mulch. The influence of organic mulch with peat and sawdust was similar to straw mulch, and least effective was grass mulch. In the study by Zaniewicz-Bajkowska et al [51] straw mulch left on the field till cabbage harvest, significantly reduced the fresh mass of weeds, on average, by 38.8 % compared to the control without mulch. In the study by Din et al [52], soil mulching with wheat straw in corn cultivation contributed to a decreased mass of weeds, on average, by 27.1 %, compared to the plot without straw. Kristiansen et al [53] were found that during echinacea (*Echinacea purpurea* Moench. L.) production, hay mulch exhibited >90 % greater weed control compared to a non-weeded control and was comparable to hand-weeding. The same experiment showed 85 % weed control by hay mulch for lettuce production, compared with 96 % control by hand-weeding. According to Derek et al [13] application of mulch several weeks after pepper transplanting can improve weed suppression later into the growing season. In turn, in the studies by Johnson et al [54] straw applied at planting time of vegetables suppressed weeds more effectively, whereas straw applied 4 weeks after planting had less effect on weeds.

In the study by Zagaroza [11], how efficient the mulch was depended on the thickness of the mulch layer on the soil surface. Hembry and Davies [18] found that weed growth still occurred at 20 Mg $\cdot$ha^{-1} of straw mulch, although there were fewer weeds. Yordanova and Shaban [49] claim that, organic mulch, irrespective of the mulch layer on the soil surface, did not provide good weed control, especially against the perennial weeds. In the study by Doring et al [55] there was no consistent effect of straw mulch on number of weeds, weed cover and above ground biomass of weeds. According to the authors the fact that weed development were not significantly affected by straw mulch is mainly attributed to the relatively low amounts of straw applied.

Ahmed et al [56] claimed that mulch with wheat straw contributed to a significant decrease in the mass of weeds, compared to the control plot, however, higher rates of mulch application controlled weeds more effectively. This is confirmed in the study by Uwah and Iwo [38], in which there was a decrease in the mass of weeds in maize cultivation when there was an increase in the grass dose applied to soil mulching. According to authors the weed dry matter yield obtained in the control, was over eleven times higher than the 8 Mg $\cdot$ ha^{-1} mulch rate and more than six times above the 6 Mg $\cdot$ ha^{-1} mulch rate.

Pests and diseases control

Mulch cover can play a neutral role or reduce the risk of insect pest attack to crop plants by preventing direct movement of insects from soil to plants, but sometimes mulch can increase the risk of insect invasion [57]. Mulching soil improves environmental conditions for soil organisms by protecting the habitat against water and wind erosion, drastic variations in humidity and temperature, and by increasing organic matter as a food source [58].

Changes in cropping systems affect insect pests and their natural enemies. Most insect populations were significantly influenced by ground cover. Organic mulches might provide hiding places to harbor populations of natural enemies [59]. In turn, Gill et al [60] were found that several insect groups, including ants, beetles and small plants feeding insects, were highest in unmulched control. The authors claim that it is possible that weeds in control plots without mulch may have led to the higher numbers of small plant-feeding insects in these plots.

According to Mohler [61] applying of organic mulch around small, succulent lettuce, brassica, or other vegetable seedlings can result in defoliation by slugs or insects, leading to poor stands or delayed establishment. However, these organisms have been observed to attack weed seedlings as well, and can reduce weed populations without seriously impacting well-established crops.

Chalker-Scott [3] state that mulches will reduce splashing of rain or irrigation water, which can carry spores of disease organisms up to the stems or leaves of susceptible species. Additionally, the populations of beneficial microbes that colonize many mulch materials can reduce soil pathogens either through direct competition for resources or through chemical inhibition. Mulch maintains an optimal soil environments, which in turn supports healthy plants that are less susceptible to opportunistic pathogens.

Mulching soils to encourage populations of indigenous, beneficial soil microbes will increase the effectiveness of biological control in managing disease [62]. According to Davies [63] application of organic mulches such as pine bark or wood chips are more effective in suppressing disease than black polyethylene mulch.

Vegetables yield and quality

Application of mulches beneficially influences soil structure, supply organic matter, reduces negative effects of wind and water erosion, decreases soil warming in summer months, resulting in an increases crop yields [34, 35, 64]. According to Gill et al [65], the increase in yield due to mulching is higher for species grown for early harvest. Increased plant growth in response to mulching has been attributed primarily to conservation of soil moisture, moderation of soil temperature, and reduced competition with turf and other plants [66]. This was confirmed in the studies by Sajid et al [34], in which plants of peas cultivated on the organic mulch with wheat straw and sawdust were higher on average by 5.54 and 7.72 cm compared to plants from control without mulch. The results were in agreement with Makus et al [67] who observed that plant height was significantly affected by different mulching material. According to the authors application of mulch increased plant height due to soil moisture conservation and reduced water stress. Soil mulching with organic mulches in the study by Awal and Khan in maize [68] and Kar and Kumar in potato [69] resulted in greater above-ground plant biomass and quicker plant development compared with non-mulched plots. Khan and Parvej [70] were found that mulching enhanced the number of ears per plant, ear height, length and diameter, tassel length, number of seed rows and 1000-grains weight compared to cultivation without mulch.

In the study by Zaniewicz-Bajkowska et al [51], application of rye straw as a mulch in cabbage and onion cultivation influenced the increase of total and marketable yield of these vegetables as compared to cultivation without mulch. In the study by Kosterna [39] all kinds of organic mulch contributed to increase in the broccoli yield and improvement its parameters. The favourable influence of organic mulches in different weather condition on the yield level was confirmed by many researches. An increased yield of tomato as the result of organic mulch application was found by Saeed and Ahmad [64] in Pakistan as well as Rahman et al [71] in Bangladesh, sweet pepper by Derek et al [13] in United States, carrot by Olfati et al [72] in Iran, potato by Kar and Kumar [69] in India and melon by Johnson et al [54] in United States. Olfati et al [72] were found that total yield, root weight and root length for plants grown with organic mulches were better than the bare soil control. However, the authors did not find significant differences in plant height, root diameter and inner and outer core diameter. Kar and Kumar [69] higher yield and better crop growth were observed in the mulched plots, which might be due to conservation of soil moisture and reduction of soil temperature by 4–6 ^{o}C compared to the non-mulched plots. In the study by El-Shaikh and Fouda [73] carried out in Libyan conditions the yield of cucumber cultivated on the soil with straw mulch was higher by 3.77 Mg · ha^{-1} compared to bare soil. However, in the study carried out by Döring et al [55] in Germany, mulch with straw applied to organically grown potatoes had no significant influence on the yield or tuber size fractions. In turn, Díaz-Perez [74] in the study regarding onion cultivation, found that yield with straw mulch was significantly lower compared to the control.

Wicks et al [75] in studies regarding corn cultivation found that, with increasing straw dose applied to soil mulching, there was increased average weight and number of cobs per plant. Similarly, the study by Uwah and Iwo [38] showed that increasing mulch dose from 2 to 8 Mg · ha^{-1} increased the height and number of leaves per maize plants. The grain yield obtained at 6 or 8 Mg · ha^{-1} rates was more than double that of the non-mulched control plots. In the study by Kosterna [76] it was found that all kinds of straw investigated in the experiment, irrespective of dose, contributed to a significant increase in the marketable yield, weight of marketable head and improved head quality compared to that achieved from cultivation without straw mulching.

The chemical composition of vegetables is genetically determined as well as being modified by factors affecting the plant during growth, and particularly climatic conditions and agro-technology practices [77]. The effect of organic mulches on the nutrients content is differentiated. In the studies by Samaila et al [78] mulch with straw contributed to increase in dry matter, protein and carbohydrate content in tomato. Similarly, the study by Najafabadi et al [79] showed that soil mulching with straw contributed to an increase of dry matter and vitamin C content in garlic bulbs. Majkowska-Gadomska et al [80] were found that mulching contributed to a significant increase in dry matter content in tomato fruits but had no influence on the ascorbic acid, total sugars and organic acids accumulation. Similarly in the study by Sekhon et al [81] significantly higher content of ascorbic acid in sweet pepper fruits cultivated in a control plot without mulch, compared to the plots with organic mulch was observed. In the study by Olfati et al [72], organic mulch applied in carrot cultivation did not have any influence on the dry matter content in roots. Parmar et al [82] were found that soil mulching with straw and dry leaves slightly reduced flesh acidity of melon but caused an increased monosaccharide and total sugars contents. Similarly, in the study by Kosterna [83] soil mulching with corn and rape straw caused an increase in total sugars and monosaccharide content in broccoli and tomato.

Conclusions

Soil mulching with organic material is an important element of integrated and ecological cultivation of plants. One of the most significant advantage of mulch is the addition of organic matter to the soil, especially by nutrient-rich mulch and a favorable effect on the physical and chemical properties of soil, and hence on crop productivity. This management system allows to reducing the application of chemical plant protection and mineral fertilizers. Mulches also suppress weed growth and contribute to reducing the use of herbicides in vegetable production. The effect of kind of mulch on crop growth can vary due to different production practices, growing conditions and crop species. According to many researches retention of organic matter on the soil surface favorable effect on the growth and development of plant and increase vegetables yield.

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MULCZE ORGANICZNE W UPRAWIE WARZYW

Katedra Warzywnictwa
Uniwersytet Przyrodniczo-Humanistyczny w Siedlcach

Abstrakt: Mulczowanie gleby jest bardzo ważnym zabiegiem w uprawie polowej. Różne materiały mulczujące mogą być użyte dla różnych gatunków roślin rolniczych i ogrodniczych w różnych warunkach klimatycznych. Głównym zadaniem ściółek organicznych jest ochrona powierzchni gleby przed wpływem niekorzystnych czynników oraz poprawa warunków wzrostu roślin uprawnych. Mulczowanie zmniejsza bezproduktywne parowanie z powierzchni gleby. Mulcz organiczny zmniejsza także erozję wodną i wietrzną gleby poprzez ochronę jej powierzchni oraz straty składników pokarmowych na skutek wypłukiwania. Ściółki zatrzymują wilgoć w glebie, pomagają utrzymać stałą temperaturę gleby, zwiększają jej porowatość i ograniczają wzrost chwastów. Główną zaletą ściółek organicznych jest dostarczanie materii organicznej i składników odżywczych nie tylko roślinom, ale także organizmom glebowym. Mulcz poprzez poprawę biologicznych, chemicznych i fizycznych właściwości gleby przyspiesza wzrost roślin oraz zwiększa plon. Celem pracy jest analiza porównawcza badań naukowych na temat korzyści i wad ściółek organicznych stosowanych w uprawie warzyw.

Słowa kluczowe: mulcz, uprawa

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ANALYSIS OF GAS BUBBLE FORMATION AT THE NOZZLE OUTLET

BADANIE PROCESU TWORZENIA SIĘ PĘCHERZYKÓW GAZU U WYLOTU Z DYSZY

Abstract: The paper presented a short literature review of theoretical models of formation of gas bubbles. On this basis, was prepare a classification of model. In the next step, experimental research was conducted, on the basis of which three were selected basic structure of the formation of bubbles. On the next step Then presents the results of experimental studies on the basis of which three were selected basic structure of the formation of bubbles. The classifications of bubble formation structures were expressed by Eötvös and Reynolds numbers. Furthermore, on this basis, were constructed a map of the structures forming bubbles. This paper presents a measurement method used for determination of parameters of bubbles forming at jet attachment from which the bubbles are displaced upward.

Keywords: bubble formation, mathematical models, bubble volume measurement

Introduction

Formation of gas bubbles takes place in devices and apparatus, in which the mass transfer takes place. The way in which gas bubbles forming has influence on the quality of the mass transfer process. Due to the complex nature of the phenomena occurring in the process of bubble formation in practice a wide variety of theoretical models have been reported. These models are applicable only to selected structures of bubble formation. Therefore the scope of the present work is to classify. This paper describes the attempt to systematize the range of specific structures gas bubbles formation in relation to the known dimensionless number (Reynold and Eötvös).

The gas bubble formation in the liquids is affected by various system parameters related to the nozzle design ,the supply system and the properties of gas and liquid. In the literature these factors are generally divided on: stand parameters (*eg* nozzle

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diameter, tank volume), system environment factors (*eg* liquid or gas properties) and operating parameters (*eg* gas flow rate, pressure, free movement of liquid) [1].

This paper describes the experimental method used to determine the shape and volume of gas bubbles formation. On the basis of experimental investigation the classification of the structures formation was carried out. Such classification facilitates selection of theoretical models in the design of equipment for gas bubble generation.

Classification of theoretical models for bubble formation

Models for gas bubbles formation from the nozzle with a single circular hole, and the gas bubbles formed flow upwards are discussed. It is also assumed that the bubbles formed in the stagnant liquid. For such assumptions in the literature are many models describing the bubbles formation.

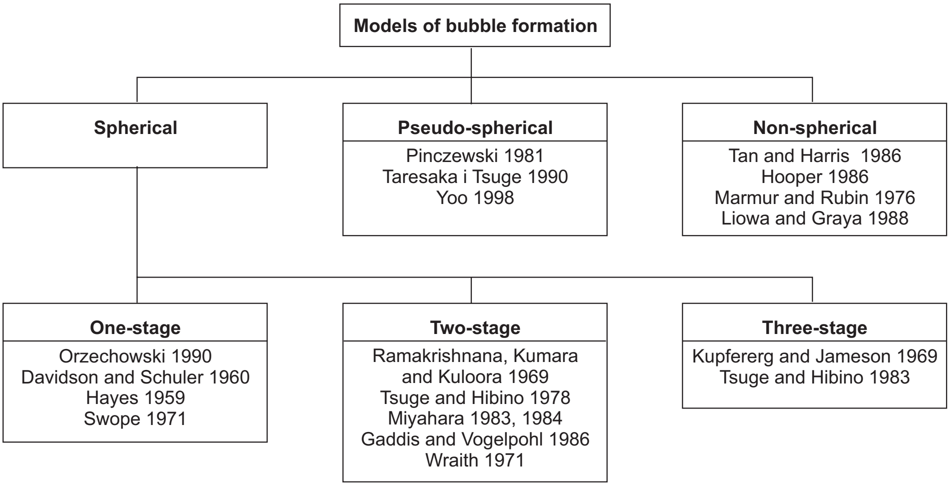

Fig. 1. Classification of theoretical model of gas bubble formation

In Fig. 1, the classification of theoretical models is proposed. Spherical models include all those arrangements, in which it is assumed that the bubbles formed are of spherical shape. Furthermore, they were divided into three groups called: one-stage, two-stage and three-stage.

This is due to the assumptions, consisting in calculating the final volume of the bubble on the basis of one, two or three phases of the bubble formation shape. One-stage models may include static models [2], which relate to very small flows, where dynamic forces are omitted. As well as dynamic models, but assuming that the bubble has a spherical shape which continuously increases in volume.

The most popular are models of Davidson, Schuler, Hayes, Swope [3–6]. Two-stage models are based on the assumption that the bubble detachment occurs in two stages. The first is the formation of a spherical bubble, followed by a second step of the bubble detaching phase. The most famous models are Ramakrishna–Kumar–Kuloora, Tsuge and Hibino, Miyahara, Gaddis and Vogelpohl and Wraith [7–12]. Three-stage models assume that after the bubble detachment from the nozzle there is for some time resting state, that the increase in the volume of residue gas at the bubble detachment is not observed. Known models are models Kupfererg, Jameson, and Tsuge and Hibino [13, 14].

Non-spherical models assume that the shape of the bubble formed is dependent on the pressure distribution on its surface. Most frequently cited models in the literature are models of Tan, Harris, Hooper, Marmur, Rubin and Liow and Gray [15–19]. Additionally, introduced division into pseudo-spherical models, which included models of Pinczewski, Taresak, Tsuge and Yoo [20–21].

Test stand

The experimental set-up used to study the bubble formation is shown in Fig. 2. The basic element is a glass column (6): 50 × 150 × 200 mm. The column is filled with water. In the bottom of the column (7) interchangeable nozzles of different shape and hole diameter are provided. The nozzle was so attached that forming bubbles were free to float to the top. Forming bubbles were illuminated by halogen lamp (5), and the image were recorded by the camera (8). DALSA camera with a resolution of 400 × 500 pixel, with image recording rate of 200 frames per second was used. Stream of gas supplied to the nozzle was controlled using a throttle valve (3), and measured by a flow meter 4. The air is produced by a membrane compressor with a tank (2). The tank volume is 5 dm^3.

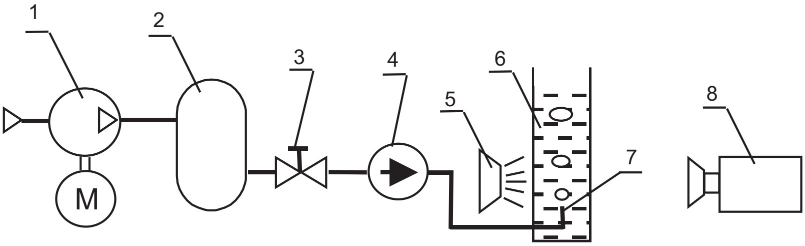

Fig. 2. The test stand

Gas bubbles were formed at the cylindrical and conical nozzles with outlet holes diameters d_0: ∅1.5 mm, ∅2 mm ∅2.5 mm, ∅3 mm, ∅4 mm (Fig. 3). Nozzles were screwed into the pressure equalizing chamber in the shape of a cylinder with an internal diameter of 45 mm and a height of 40 mm. The holes lengths in the nozzles were greater than 10 d_0, what ensures the stabilization of the gas flow. The use of two types of nozzles is to estimate the impact of changes in the liquid circulation around the bubble formed. In these two cases, the fluid flows from the bottom of the bubble formed at different angle. This results in a changing impact of dynamic forces associated with the liquid inernest.

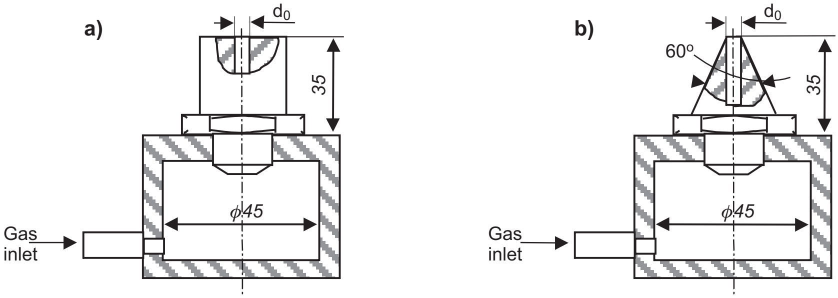

Fig. 3. The construction of nozzles for gas bubble generations a) cylindrical; b) cone

Results of observed the shape of bubble formation

Images recorded on the camera were subjected to image analysis based on which is possible to determine the characteristic parameters of the gas bubbles formation. Image of the gas bubbles recorded by camera is the image in 256 shades of gray. In practice, it is easier to analyze the shape of the bubble, when it is a distinct phase of gas and liquid. For this purpose, the camera images were subjected to Image Processing of image binarization [23].

To carry out the process of image binarization software Vision with the program LabView 7.1. was used. Images from the camera are subject to certain defects, such as reflections of light, different kinds of shadows and reflections. This causes that an image taken directly from the camera is not suitable for further analysis, it requires the appropriate image processing. An exemplary image is shown in Fig. 4a.

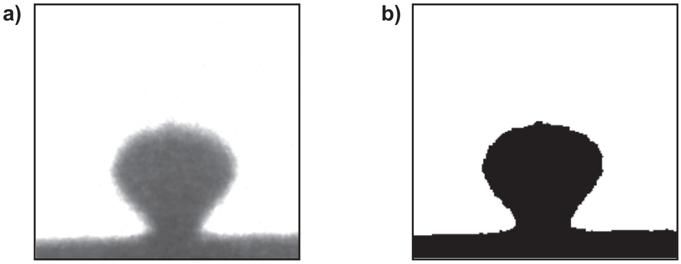

Fig. 4. Images of bubble a) from video camera; b) after binearyzation

Individual images were processed to brightness and improvement of contrast. In order to improve, the quality of the separation of bubble contours color inversion is performed. For such crafted image, image transformation is done on a one-bit map (Fig. 4b). As a consequence the transformation of the image is obtained, in which each pixel is assigned value 1 or 0. This corresponds to occurring a gas or liquid in a given location.

In Fig. 4a a white color represent the liquid, and black is for the gas. In order to remove of artifacts that arise in the image processing, the selective removal of small objects was used. This operation involves the removal of objects whose size exceeds a threshold value. This value was chosen experimentally. At the end of the binarization process the empty space inside the bubbles was filled.

For such processed images shape of gas bubbles formated were analyzed. Three basic structure of the gas bubbles formation were separated (Fig. 5). Individual changes in the structure of gas bubbles formation are referenced by dimensionless number taking into ccount stand factors, the operating and design parameters. ne of the dimensionless numbers that takes into account the diameter of the nozzle, the flow rate of gas and rheological properties of the liquid is the Reynolds number. This number is defined as follows:

$$\mathrm{Re} = \frac{v d \rho_c}{\eta_c} \tag{1}$$

where: d – nozzle diameter [m],
ρ_c – liquid density [kg/m^3],
η_c – liquid viscosity [Pa · s],
v – average gas velocity [m/s].

The observed results shows that video sequences of bubbles formation correlate well with the theoretical models of the gas bubbles formation division (Fig. 1), which are divided into spherical models that assuming spherical shape of the bubble, pseudo-spherical taking into account the equations of motion and non-spherical taking into account the dynamic forces of equilibrium. Characteristic ranges for passage of structures of bubbles formation are the value of the Reynolds number. For a conical nozzle having a hole diameter of 3 mm at a gas flow Q < 10 cm^3/minute (Fig. 5a) the shape of the bubble formated is close to a sphere. Detachment of the bubble from the nozzle occurs at the dominance of static forces and the shape of the bubble during detachment is only slightly deformed.

For this structure for numerical calculation can be successfully used spherical models. For the same nozzle, but to the flow Q = 10 – 150 cm^3/min transition structure

Fig. 5. Typical struktures of bubbles formations a) spherical; b) pseudo-spherical; c) no spherical

is formed, characterized by pseudo-spherical shape of gas bubbles formed (Fig. 5b). The characteristic is spherical bowl with a clear narrowing portion cylindrical. This shape very well approximate the theoretical models classified as pseudo-spherical (Fig. 1). For streams Q > 150 shapes of bubbles formation are irregular (Fig. 5c), their shape resembles the shape of the fungus. There is no shape repeatability during successive bubbles formation. For this structure seems to be a reasonable use of non-spherical models for numerical simulation. Ranges of values for Reynolds numbers for nozzles with different hole diameters take different values.

Measured of bubbles volume

Reconstruction and thereby determination the volume of the bubble detachment volume is to approximate the shape of a series of cylinders (Fig. 6a). The values of each diameter of the base of the cylinder is determined based on the binary image bubble (Fig. 6b). The diameters are calculated on the basis of the number of pixels in a given line of an image, then based on the pixel value in millimeters. A succession of diameters are measured with a constant step size of one pixel, and base on it the height of the cylinder *h*.

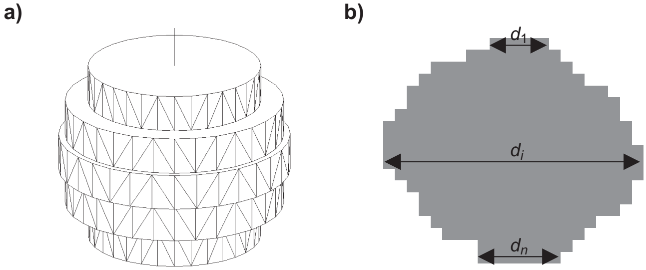

Fig. 6. Bubble volume calculation a) idea of bubble shape reconstructions; b) calculation of cylinder diameter

The volume of the bubble is the sum of the cylinders volumes making up the bubble. For the approximation of the bubble shape by elliptical cylinder, the formula for the volume takes the following form:

$$V = \sum_{i=1}^{n-1} V_i = \frac{h\pi}{4} \sum_{i=1}^{n-1} d_i^2 \tag{2}$$

where: V_i – volume of one cylinder [m^3],
d_i – diameter of cylinder [m],
h – height of the cylinder [m],
n – numbers of cylinders.

Example of bubbles images are shown in Fig. 7. The error of the shape reconstruction and the precision of the designation of volume largely depend on the

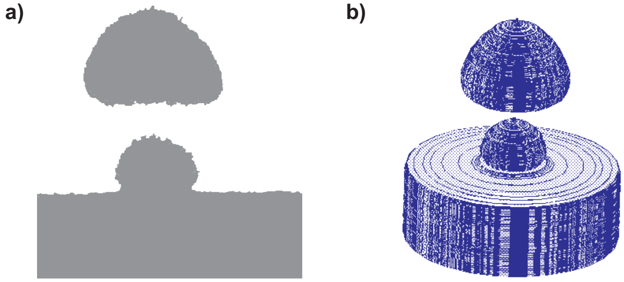

Fig. 7. Reconstruction of buble shape a) image of bubble after binearization; b) 3D images after reconstruction

bubble image resolution. The shape reconstruction of the bubbles formed not only allows the calculation of its volume, but allows analysis of changes in the shape. Such an analysis is essential for verification of theoretical models of gas bubbles formation.

Test results

Based on the volume measurements of bubbles formation, the limits for the dimensionless quantity at which a change the structure of the bubble formation is occurs, was set. The dimensionless quantity should take into account stand, system and environmental factors (operating and design parameters). One of the dimensionless numbers, that takes into account the diameter of the nozzle, the gas flow rate and liquid rheology is the Reynolds number.

Taking into account the environmental factors of the process, results were referred to the Eötvös number. It takes into account properties of the liquid and gas and the diameter of the gas bubbles detaching. This number is defined based on the equivalent bubble diameter. The equivalent diameter de is taken as the sphere diameter that has the same volume as the bubble that separated from the nozzle. Eötvös number was calculated by the formula:

$$Eo = \frac{g\,(\rho_c - \rho_g\,)\,d_e^2}{\sigma_c} \tag{3}$$

where: d_e – equvialet buble diameter [m],
ρ_g – gas density [kg/m^3],
σ_c – surface tension coefficient [N/m],
g – acceleration of gravity [m/s^2].

Afterwards, attempted to determine the map of gas bubbles formation. The bubble formation maps expressed by Eötvös and Reynolds numbers were constructed. Figure 8 shows the results of gas bubbles formation for two different nozzles. Individual points marked with circles in the graph represent the structure of a spherical bubble formation. The triangles are for pseudo-spherical structure, and squares represent a non-spherical

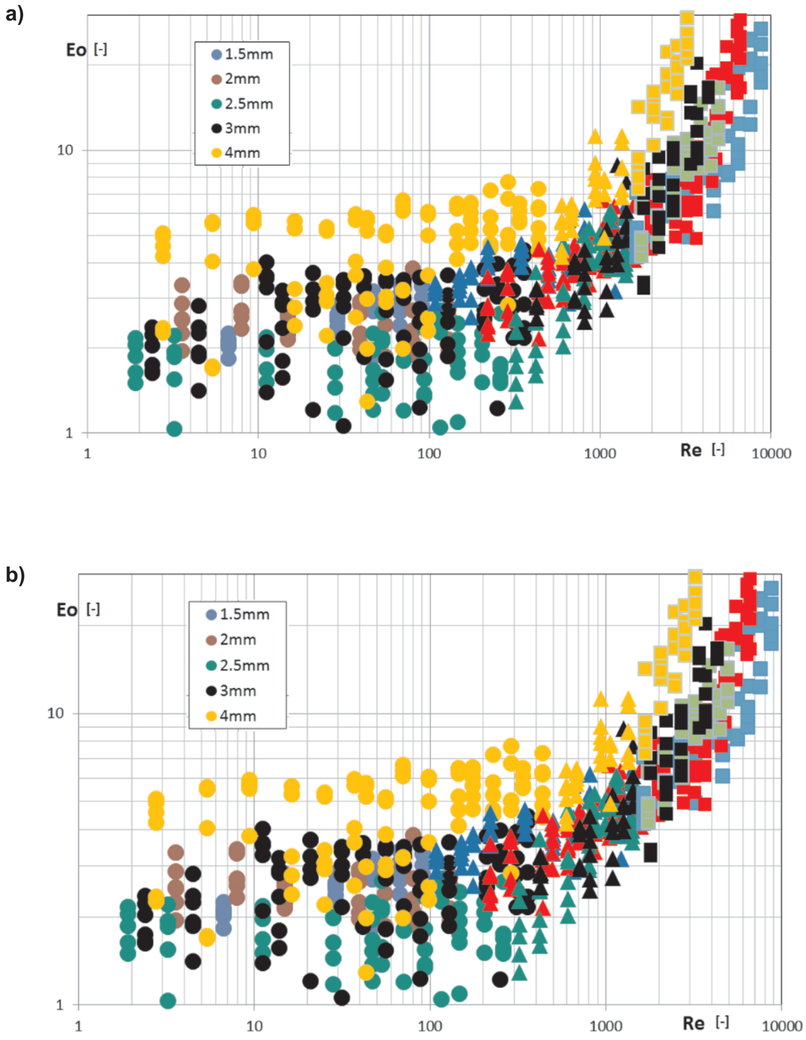

Fig. 8. Maps of gas buble formation for a) cylindrical nozzle; b) core nozzle

structure. Different colors denote values of the gas flow coming out from the nozzle. As shown by the presented maps for the cylindrical nozzle (Fig. 8) spherical structure formed at Reynolds numbers under 300. As indicated Reynolds numbers in the range from 300 to 1500 represent the formation of a pseudo-spherical structure. Further, for the Reynolds number higher from 1500 a pseudo-spherical is created. For a spherical structure Eötvös numbers assume a constant value. However, for non-spherical structures a rapid increase in Eötvös number was observed. As Eötvös number is defined by the bubble diameter, this means that in spherical structure formation the gas flow rate does not significantly affect the final volume of the bubble. It affects only the frequency of their formation. On the other hand, not spherical structure has a completely different nature, here the gas flow velocity is crucial for the final volume of the bubbles. The influence of the nozzle shape for the range in which individual structures are formed is small. For example, for a conical nozzle spherical structures are formed for Reynolds numbers less than 200 while the chain structure is formed at Reynolds numbers above 1500. Compared with the cylindrical nozzle intervals are very similar. In addition a great similarity of the Eötvös numbers was observed.

Conclusions

In this work, the phenomena of bubble formation were investigated. The effect of different parameters on the regimes of bubble formation and their transition was investigated experimentally. It has been shown that forming bubbles can be divided into three basic structures. The maps of gas bubble formation base on Reynolds and Eötvös number were proposed. Finally, on this basis it is possible to determine the limits of Reynolds numbers at which a change in the structure of the formation of bubble is occurred. The ranges reported in present work are expected to facilate design of equipment and machines in which there is formation of gas bubbles.

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BADANIE PROCESU TWORZENIA SIĘ PĘCHERZYKÓW GAZU U WYLOTU Z DYSZY

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Abstrakt: Praca zawiera krótki przegląd literaturowy modeli teoretycznych tworzenia się pęcherzyków gazu. Na tej podstawie przeprowadzono klasyfikację modeli. Następnie przedstawiono wyniki badań eksperymentalnych, na podstawie których wyłoniono trzy podstawowe struktury tworzenia się pęcherzyków. Klasyfikacje struktur oparto na liczbach kryterialnych Reynoldsa oraz Eötvösa. Posłużyło to do opracowania map struktur tworzenia się pęcherzyków. Ponadto w pracy przedstawiono metodę pomiarową do wyznaczania objętości tworzących się pęcherzyków gazu.

Słowa kluczowe: tworzenie pęcherzyków gazu, modelowanie matematyczne, pomiar objętości pęcherzy

Indexes

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WYKAZ AUTORÓW PUBLIKACJI ZAMIESZCZONYCH W TOMIE 21 KWARTALNIKA „ECOLOGICAL CHEMISTRY AND ENGINEERING A / CHEMIA I INŻYNIERIA EKOLOGICZNA A”

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

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

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ZAPRASZAMY DO UDZIAŁU W ŚRODKOWOEUROPEJSKIEJ KONFERENCJI ECOpole ’15

SUBSTANCJE CHEMICZNE W ŚRODOWISKU PRZYRODNICZYM

w dniach 14–17 X 2015 r. w hotelu Ziemowit w Jarnoltówku

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

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