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Jolanta KOZŁOWSKA-STRAWSKA[1] and Adam KACZOR[2]

SULPHUR AS A DEFICIENT ELEMENT IN AGRICULTURE – ITS INFLUENCE ON YIELD AND ON THE QUALITY OF PLANT MATERIALS

SIARKA JAKO PIERWIASTEK NIEDOBOROWY W ROLNICTWIE – ROLA W PLONOWANIU I WPŁYW NA JAKOŚĆ SUROWCÓW ROŚLINNYCH

Abstract: Sulphur plays a special role in plant metabolism. It takes part in protein synthesis and sugar metabolism and influences the quantity and quality of fat in seeds, the quality of wheat flour, the value of hay as fodder, and the taste and smell of onion and garlic. Because of its functions in the life of plants, sulphur can be included alongside nitrogen, phosphorus and potassium as a nutrient determining crop yield and quality. The role of sulphur in plant nutrition has gained importance in the last 10–15 years, when this nutrient was found to be deficient in plant production in most European countries, including Poland. This was mainly due to the reduction in emissions of sulphur compounds to the atmosphere and in the amount of sulphur entering the soil with mineral and natural fertilizers. This element's functions and its increasingly severe deficiency in the growth environment of plants indicates that sulphur should be considered alongside other nutrients in determining the fertilization requirements of crop plants.

Keywords: source of sulphur, sulphur in plants, quantity of plants, quality of plants, sulphur as a deficient nutrient

Introduction

Sulphur has long been known to be an essential nutrient for the proper development of living organisms. In considering the quantitative nutrient requirements of plants, sulphur is usually placed fourth, after nitrogen, potassium and phosphorus [1].

Sulphur plays a special role in the metabolism of plants. It is a component of many important compounds whose deficiency leads to disruptions in plant development [2–5].

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[1] Department of Agricultural and Environmental Chemistry, University of Life Science in Lublin, ul. Akademicka 15, 20–950 Lublin, tel. 081 445 60 18, email: jolanta.kozlowska@up.lublin.pl

[2] Department of Biochemistry and Environmental Chemistry, Faculty of Agricultural Sciences in Zamość, University of Life Science in Lublin, email: adam.kaczor@up.lublin.pl

In spite of its importance, until the early 1980s little attention was given to sulphur in European countries. It was not a subject of interest in agricultural research, nor was it taken into account in determining the fertilization requirements of plants. This was due to the fact that on most of the continent the sulphur balance was positive. The main contributor to this positive balance was SO_2 emitted into the atmosphere during burning of fuels, particularly hard coal, brown coal and petroleum. Significant amounts of sulphur also entered the soil with certain mineral fertilizers [1, 6–8].

Excessive emissions of sulphur compounds had a negative influence on ecosystems and on the quantity and quality of plant materials [9–11]. The damage was so great that numerous measures were taken to reduce the amount of sulphur oxides in the atmosphere. These measures were so effective that SO_2 emissions were reduced by 40–60 % in most countries [12].

Unfortunately, the reduced amounts of sulphur present in the atmosphere and entering the soil with mineral fertilizers led to sulphur deficiencies in plant production [4, 6, 7, 13–16].

There are many indications that in some regions of Poland the sulphur balance in the soil may be negative as well. Studies by IUNG, Pulawy assessing the amount of sulphur in our country's soils suggest that this element may be lacking in the growth environment of plants [15]. These data show that in over half of soils (53 %) the supply of sulphur available to plants is low (less than 20 mg $S\text{–}SO_4 \cdot kg^{-1}$), in 26 % average, and in 16 % high. The remaining 5 % are soils polluted due to human activity. Deficiency of this nutrient can be expected mainly in lighter, usually acidified mineral soils, situated far from industrial centres [3, 8, 12].

Sulphur deficiencies, as a new problem in agriculture, become apparent mainly in crops whose demand for this nutrient is high, and are manifested as a decrease in yield (by as much as 50 %) and lower quality of agricultural produce [1, 6, 7, 17].

The aim of this study is to assess the role of sulphur as a deficient nutrient in determining the yield and quality of crop plants. The assessment will be made on the basis of data from the literature and in part on the authors' own research.

Sulphur sources in agrosystems

The primary sources of sulphur in the soil are minerals. The most important of these are gypsum ($CaSO_4 \cdot 2H_2O$), iron sulphides (FeS and FeS_2), hydrotroilite ($FeS \cdot nH_2O$), sphalerite (ZnS), chalcopyrite ($CuFeS_2$), cobaltite (CoAsS), sodium aluminium sulphate ($NaAl(SO_4)_2 \cdot 12H_2O$), tamarugite ($NaAl(SO_4)_2 \cdot 6H_2O$), iron sulphate ($FeSO_4$), potassium sulphate ($K_2SO_4$), sodium sulphate ($Na_2SO_4$), and magnesium sulphate ($MgSO_4$), as well as compounds in a lower oxidation state, such as sulphites, thiosulphites, pentathionates and elemental sulphur [9, 17].

Most sulphur, however, occurs in the form of organic compounds and is a component of humus. The remaining organic compounds enter the soil together with plant and animal residues and microorganisms. Dominant among these are the following:

– amino acids, especially methionine and cysteine,
– peptides (glutathione),

– proteins,
– sulpholipids,
– vitamins – thiamine and biotin [2, 9, 15].

Sulphur also enters the soil with certain mineral fertilizers. These can contain chemically diverse forms of sulphur, so that their assimilability varies considerably [1, 7, 8, 13, 16, 18, 19].

The mineral fertilizers which introduce the greatest amounts of this element into the soil are ammonium sulphate (240 kg S · Mg^{-1}), potassium sulphate (180 kg S · Mg^{-1}), single superphosphate (120 kg S · Mg^{-1}), gypsum or phosphogypsum (180–190 kg S · Mg^{-1}), magnesium sulphate (130 kg S · Mg^{-1}), kieserite (220 kg · S Mg^{-1}) and elemental sulphur [1, 11, 13, 15].

Certain amounts of sulphur can also enter the soil with natural fertilizers, especially manure, in which the sulphur content ranges from 0.3 to 0.6 kg S · Mg^{-1} [1, 13, 17, 20].

In recent years the amount of sulphur entering the soil in the form of mineral and natural fertilizers has undergone a marked decrease. This problem concerns not only Poland, but some other European countries as well. In Denmark, for example, 34 kg S · ha^{-1} · $year^{-1}$ entered the soil with these fertilizers from 1970 to 1975, but only 20 kg S by 1994 [7, 14, 15, 20]. In Poland, with the current level of mineral fertilization and assortment of mineral fertilizers used, about 10 kg S · ha^{-1} · $year^{-1}$ are estimated to enter the soil in this way. The amount of sulphur introduced into the soil by manure should be added to this figure.

Certain amounts of sulphur can make their way into the soil from the polluted atmosphere through dry deposition or wet deposition [1, 7, 9, 17]. Dry deposition occurs when SO_2 is absorbed on the soil surface in gas form, and then dissolved and oxidized in the soil solution. Sulphur oxides can also be oxidized to sulphuric acid in the atmosphere and make their way into the soil with rain or other precipitation. Then we are dealing with acid rain [3, 10, 21]. The main source of SO_2 emissions is electricity production, which is responsible for nearly 57 % of all sulphur oxides emitted into the atmosphere. When industrial power and systems for supplying heat to the household and public sector are taken into account, the figure reaches nearly 95 %.

Compared with 1980, when annual sulphur oxide emissions in Poland reached 4132 thousand metric tonnes (ie Mg), a marked decrease has been noted [8, 11, 12, 20]. A major reason for this was the Oslo Protocol signed in 1994, under which Poland committed itself to limit its SO_2 emissions to 1397 thousand metric tonnes by 2010.

In western and northern Europe, a decrease in sulphur oxide emissions took place as early as the early 1980s [4, 16]. A significant reduction of SO_2 in the atmosphere in Europe resulted from the Helsinki Protocol signed in 1985, under which the signatories committed themselves to reducing emissions of sulphur compounds by 30 % by the end of 1993. Further decisions required that by 2003 reduction of SO_2 emissions would reach 60 % [6, 16].

Some authors [9], however, emphasize that in spite of the significant decrease in SO_2 emissions, they are showing a clear tendency to rise again. According to these authors, the main reason for this tendency is the overly energy-intensive structure of our economy and the high share of hard coal and brown coal in the country's fuel-energy balance.

Sulphur uptake mechanism

Plans take up sulphur through their roots, mainly in the form of SO_4^{2-}. Certain amounts of the element can also be absorbed by leaves in the form of SO_2 [2, 11, 17, 22].

The sulphate uptake mechanism can be passive or active. The passive process is physicochemical, mainly taking place through diffusion, and consists in an equalizing of concentrations between the external solution and the apparent free space in the root. Sulphates within this space are not bound and can be exchanged for other ions or removed by scrubbing. The active sulphur uptake process can take place against the concentration gradient and requires energy expenditure by live cells [2, 17].

Sulphur can also be taken up by plants in the form of SO_2 [1, 17]. Of the total sulphur content in plants, the proportion which is taken from the air depends on how well-supplied they are with this nutrient. On average the proportion is taken to be 15–30 % in plants well-supplied with sulphur, and more than 50 % in plants suffering from a deficiency of this element. From these data it can be concluded that sulphur contained in the air cannot be a sufficient source of this nutrient for plants.

Sulphate uptake depends on many external factors. One of these is ion concentration [3, 8, 11, 13, 23]. The higher the concentration of SO_4^{2-} ions in the external environment, the greater their uptake by plants. Of course this effect has limits, depending largely on the species of plant cultivated. After these values are exceeded, further increases in sulphate ion concentration no longer affect how quickly the ions are taken up by plants.

The presence of other ions in the plant growth environment can also affect sulphur uptake. Nitrogen and phosphorus play an indirect role resulting from the fact that in determining crop yields, they also increase the need for other nutrients, including sulphur [7, 8, 24, 25].

Calcium and magnesium ions, on the other hand, cause a marked decrease in sulphur content in plants [1, 26, 27]. In experiments with meadow grasses and maize, the authors cited demonstrated a 5–25 % decrease in sulphate content in plants fertilized with magnesium chloride. A similar tendency was observed after soil liming with dolomite.

A marked antagonism was also observed between the uptake of selenates and sulphates [28]. This dependency occurs in higher plants as well as in algae and fungi. In the case of higher plants, however, sulphates are taken up more intensively than are selenates.

The rate of sulphate uptake also depends on the vegetative stage of the plant. Generally most of the sulphur is taken up during the period before blooming [4, 13, 20]. During later developmental stages the percentage content of sulphur in the plants decreases. This is due to a rapid increase in dry plant weight and a decrease in the rate of sulphur uptake.

Sulphur requirements of plants

The sulphur requirements of plants depend mainly on its species and on crop size [4, 6, 13, 15, 17, 20, 29, 30]. Sulphur demand in particular plant species is generally similar to phosphorous demand. Grasses, however, and thus grains and maize as well, take up less sulphur than phosphorus; the Fabacae take up similar amounts; while the Brassicaceae and the Liliaceae take up more sulphur than phosphorus.

Crop plants can be divided into three groups according to their sulphur requirements [9, 11, 17]:

I. Plants with very high sulphur demand. This group consists mainly of the Brassicaceae, such as rapeseed, mustard, radish and turnip, and the Liliaceae, such as onion and garlic. These plants produce specific sulphur compounds which determine their quality characteristics, such as fatty acids, mustard oil, and others. With an average yield they take up 40 or even 80 kilograms of sulphur from 1 ha. Plants belonging to this group respond to an addition of sulphur to their environment with a marked increase in yield [6, 8, 15, 18, 22, 29, 31, 32].

II. Plants with high sulphur demand. These include mainly the Fabacae, particularly alfalfa and clover, which produce significant amounts of protein, as well as maize and beets, due to the quanity of biomass produced. In the case of the Fabacae, their high sulphur requirements are also the result of symbiosis with bacteria binding nitrogen from the air [4, 13, 17].

III. Plants with relatively low sulphur demand. The nutritional requirements of this group of plants range from 12–25 kg of sulphur from 1 hectare. This group includes various grass species as well as potatoes. In these plants, even in soil very rich in sulphur there is generally no response to fertilization with sulphur alone. However, when they are fertilized with high levels of other nutrients, particularly nitrogen and phosphorus, causing yields to rise, there may be an increase in sulphur demand and in the response to sulphur added to the growth environment [7, 15, 25].

Symptoms of sulphur deficiency in plants

External symptoms of sulphur deficiency are difficult to identify. In many cases they are nearly identical to those of nitrogen deficiency [1, 6, 8, 13, 17, 33]. The only difference is that lack of nitrogen first manifests on older leaves, which yellow and then dry up, while with sulphur deficiency the yellowing appears on younger leaves and apical meristem. Typical symptoms of sulphur deficiency in the growth environment of plants are small, light green leaves and shortened and narrowed leaf veins, somewhat lighter than the tissue between the veins.

In some plants, such as rape, swede, and turnip, along with yellowing there appears a characteristic curling of the leaf blade to form a spoon shape [2, 8].

Under conditions of sulphur deficiency plants also produce less chlorophyll, and if the deficiency is severe, chloroplast disintegration occurs in their assimilative organs [5].

Other symptoms can be observed when sulphur is lacking in the growth environment of plants, such as changes in leaf and stem colour and improper development of some organs [6, 17]. Numerous studies of rape, which is particularly sensitive to sulphur deficiency, have found growth to be inhibited in plants living in conditions where this nutrient was lacking. When stem or leaf growth is inhibited, plants are undergrown and the surface area of the leaf blades decreases, reducing the assimilative surface. Plant habit is altered as well, as stem thickness growth is inhibited. As sulphur deficiency becomes more severe, the leaves and stems because stiff and brittle [2, 17].

Similar dependencies have been found in studies by these authors on direct and secondary effects of sulphur fertilization and liming on crop yield [34]. From observations made during vegetation it can be concluded that one of the factors inhibiting the development of the Brassicaceae and grain species studied was sulphur deficiency in their growth environment. The Brassicaceae (rape, mustard plant) had altered plant habit and numerous deformations, while the grains (especially spring barley) had markedly lower propagation rates and produced fewer ears than plants whose fertilization included sulphur.

Influence of sulphur on crop yield

Sulphur is a nutrient which plays a major role in determining crop yield. Its deficiency generally leads to lower yields, particularly in plants that are highly sensitive to lack of sulphur in their growth environment. Reduced yields can also result from direct and indirect effects of sulphur compounds emitted into the atmosphere in large quantities [9, 10, 16, 20].

Numerous experiments conducted in Great Britain, Ireland and many other countries indicate a marked increase in the yield of crops fertilized with sulphur [4, 6–8, 15, 16, 18, 31, 32, 35, 36]. This is particularly true of rape and of grasses cut several times a year.

The results of field experiments conducted with various plants in Great Britain indicated that sulphur fertilization increased rape yield by 10–327 %, while in the case of grasses cut several times a year the increase in biomass produced was 5–134 % compared with the control [1, 5, 13]. It should be noted, however, that the response of rape to sulphur fertilization varied considerably. In one of the experiments conducted in an industrial area of England, where the rape yield was 2 $Mg \cdot ha^{-1}$, application of 10 $kg S \cdot ha^{-1}$ led to a marked increase in yield, whereas in agricultural regions of Scotland with a yield of 3.5 $Mg \cdot ha^{-1}$ the maximum increase in seed yield was observed only after application of 32 $kg S \cdot ha^{-1}$. These observations showed that the optimal dose of sulphur, ensuring maximum winter rape yields, should be within a range of 20–30 $kg S \cdot ha^{-1}$ [13, 37]. Studies conducted in Poland have increasingly emphasized that the sulphur demand of the new, doubly-improved varieties of rape is 88 kg S where seed yield is 3.5 $Mg \cdot ha^{-1}$ [20, 30, 32].

Research by Withers et al [36] and Scherer [1] showed that grains, which have lower sulphur requirements, responded with a maximum yield increase to much lower doses of this nutrient. The optimal dose for barley was 10 $kg S \cdot ha^{-1}$ in the form of gypsum, while for wheat it should be about 20 $kg S \cdot ha^{-1}$. At this level of sulphur fertilization, the increases in grain yield for winter forms of wheat and barley were 4–18 %, while straw yield increased 1–16 %.

In the case of meadows cut several times a year, experiments conducted in Wales and in southwest England determined that the most effective dose was about 10 kg S · ha^{-1} for each cut [13]. Similar dependencies were found in other studies [6, 31, 38].

As in other countries, many studies have been conducted in Poland on the influence of sulphur on crop yield. One of the first of these was carried out in 1914 by Wróblewski, who used elemental sulphur in potato and rape cultivation [cited by 39]. Koter et al [40], in experiments using the isotope ^{35}S observed a marked increase in the vegetative mass of spring rape, oats and Swedish clover when sulphate concentration was increased. Goźliński and Grzesiuk [cited by 9], found in their experiments with maize that when sulphur is deficient there is no grain yield, because only rudimentary ears are formed. A similar response is found in beans, which do not form pods when sulphur is lacking.

Later, Benedycka [41] demonstrated the beneficial effects of sulphur fertilization (K_2SO_4) on common radish grown in light soil. Similarly, in an experiment with sunflower and seradella, Uziak and Szymańska [24] confirmed that applying sulphur to the growth environment was highly effective. In the case of sunflower, the positive effects of increased sulphur occurred following application of a higher level of NPK fertilizer, while for seradella, the higher sulphur dose negated the unfavourable effects of a large concentration of NPK on yield.

An excess of sulphur can also affect crop yield, but because sulphur is currently considered a deficient element in agriculture, the problem of excessive amounts of sulphur on cultivated plant yield will not be considered in this paper.

Distinct differences in growth and development were also observed between various species in a study conducted by these authors [34]. The greatest increase in yield resulting from application of sodium sulphate in the first year of the study occurred in the case of spring rape, spring barley and white mustard, while oats responded with the lowest increase. The least response to sulphur fertilization was observed in oats. This is closely correlated with the nutritional sulphur requirements of particular plant species.

The influence of sulphur on the quality of crops

In addition to the influence of sulphur on yield, emphasis has also been placed on its effects on the quality of plant material obtained [4, 6, 7, 13, 25, 32, 33, 42]. The main effect of sulphur deficiency is that it limits protein synthesis. The role of sulphur in the synthesis process consists of two fundamental functions:

1. Sulphur is an essential nutrient for the proper activity of enzymes involved in nitrate reduction, hence plants grown in conditions where this element is lacking accumulate nitrogen in non-protein form (nitrates, amides, and other compounds, such as ammonia).

2. Plants lacking sulphur produce lower-quality protein, with lower content of exogenic amino acids, particularly methionine and cysteine [2, 7, 9, 11, 17].

An insufficient supply of sulphur to plants also causes changes in sugar metabolism. A two- or threefold increase in starch content occurs, while at the same time the amount of reducing sugars decreases. This is mainly because of decreased photosynthetic activity in the plants due to chlorosis induced by the lack of sulphur [1, 11].

In oilseed crops, sulphur deficiency usually leads to decreased fat content in the seeds [6, 8, 9, 29, 32, 42]. This problem most severely affects rape. Sulphur strongly increases both this plant's yield and the fat content of its seeds. Experiments conducted by numerous authors [13, 37] show that a dose as low as 25 kg $S \cdot ha^{-1}$ causes an increase of about 20 % in the oil obtained from 1 hectare, compared with plants that were not fertilized with this nutrient.

Nevertheless, it is worth mentioning that in the opinion of some authors [5, 30, 42] increased accumulation of oil in rape seeds is accompanied by an increase in free fatty acid content, which results in significantly poorer quality of the oil. For this reason the amount of sulphur applied to the soil should be strictly correlated with the plants' demand for this nutrient. Exceeding the recommended amounts reduces the technological value of the oil by increasing its acidity [9, 13, 42].

Sulphur fertilization is also one of the most important factors affecting the synthesis and accumulation of glucosinolates in rape seeds [1, 6, 8, 13, 29, 32, 42]. Excessive amounts of these compounds negatively affect the quality of post-extraction ground meal so that it cannot be used as fodder. According to McGrath et al [13] about 25–30 % of the total amount of sulphur present in seeds occurs in glucosinolates, which negatively affects the taste of post-extraction ground grain and increases goitrogenic activity in animals.

Also very important in terms of quality of plant materials is adequate supply of sulphur to grains. Sulphur deficiency leads to reduced quality of wheat flour by negatively affecting its "baking value" [6, 13, 25, 27, 33]. This has to do with the positive correlation between sulphur content in flour and plasticity of dough [7, 13, 25]. This problem affects both conventional and organic agriculture, because substances enhancing the baking value of flour should not be added to organic products [6, 11].

Another negative effect of sulphur deficiency in the growth environment of plants is reduced fodder quality of hay [1, 6, 17, 31]. Sulphur deficiency increases nitrate concentration in meadow plants, while a high level of sulphur fertilization of grasslands leads to significant limitation of selenium intake by plants. Animals feeding on such fodder are less able to assimilate copper contained in it.

Seeds of plants from the Fabaceae family, which are a valuable source of protein for people and animals, also require proper levels of sulphur fertilization. When lacking in this nutrient, they produce protein with markedly lower content of sulphur amino acids, particularly methionine, which is one of the most valuable amino acids determining the nutritional value of plants [1, 13, 17].

The beneficial effects of sulphur on crop quality are also noticeable in the case of vegetable crops. The main benefits of sulphur fertilization of these crops are increased carotene content and improved taste and smell of onion and garlic [9, 22].

In studies conducted by these authors, application of sulphur in the form of Na_2SO_4 also had a marked effect on the quality of the species studied [43]. In the case of rape, an increase in fat content was observed, with a lower proportion of linolenic acid. This should be considered a beneficial characteristic, because too much of this fat accelerates the rancidity process. An unfavourable consequence of sulphur fertilization, in terms of the quality of edible vegetable fats, is the decreased proportion of linoleic acid observed in the seeds of plants fertilized with sulphur. In the case of white mustard seeds, application of sulphur had a relatively small influence on total fat content, but the quality of the fat obtained was noticeably improved. This was manifested as an increase in the proportion of oleic acid, and in some sites, of linolenic, myristoleic and palmitoleic acids. Higher content of these unsaturated acids in industrial fats improved their properties significantly. In the case of grain crops, the beneficial effects of sulphur fertilization was manifested as an increase in the percentage of valine in barley grain and of tyrosine and phenylalanine in oat grain.

Determining the level of nutrient supply in plants

In terms of yield and crop quality, it is very important to determine the level of nutrient supply. This also has great importance in examining economic and ecological aspects, because under conditions of optimal macro- and micronutrient supply, fertilization is highly effective and relatively small quantities of nutrients are transported outside the root system [1, 16, 17].

The most frequently used sulphur indicators in plants are total S content, N:S ratio, S-SO_4 content and the ratio of sulphates to total sulphur [1, 6, 7, 11, 13, 33, 37]. The choice of indicator should be determined mainly by the species of the plant whose sulphur supply is to be assessed. According to numerous authors [13, 25] the best indicator for determining sulphur supply in grasses is the N:S ratio. With optimal sulphur supply to this group of plants the ratio should be about 17:1. Other indicators, such as total sulphur content, sulphates, and total nitrogen, are highly variable during plant vegetation, and thus are less reliable in assessing the plant’s supply of this nutrient. This view was supported by studies by Rasmussen, Spencer and Freney (cited in [13]), who suggested that the N:S and sulphate to total S ratios are constant throughout the vegetation period. Recently, however, it has been demonstrated that virtually all of the indicators used take on different values during different development stages of plants. This variability makes them difficult to use in assessing the sulphur nutrition status of plants [4, 11, 13].

The best indicator for winter rape harvested in the bloom stage is considered to be total S concentration, where the critical value indicating sulphur deficiency is 4 mg $S \cdot g^{-1}$ dry weight. The N:S ratio in leaves is considered less useful because it has a straight-line correlation with seed yield, making it impossible to determine a critical value for it [8, 13].

The N:S ratio is, however, the best indicator for assessing sulphur deficiency in hay. The critical value of this ratio, according to Richards (cited in [13]) is taken to be 20:1.

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SIARKA JAKO PIERWIASTEK NIEDOBOROWY W ROLNICTWIE – ROLA W PLONOWANIU I WPŁYW NA JAKOŚĆ SUROWCÓW ROŚLINNYCH

Katedra Chemii Rolnej i Środowiskowej Uniwersytetu Przyrodniczego w Lublinie
Katedra Biochemii i Chemii Środowiska,
Wydział Nauk Rolniczych w Zamościu, Uniwersytet Przyrodniczy w Lublinie

Abstrakt: Siarka odgrywa specyficzną role w metabolizmie roślin. Bierze udział w syntezie białek, metabolizmie cukrów, wpływa na ilość i jakość tłuszczu w nasionach, decyduje o jakości mąki pszennej, wartości paszowej siana oraz walorach smakowo-zapachowych cebuli i czosnku. Funkcje, jakie pełni ten pierwiastek w życiu roślin, pozwalają zaliczyć go obok azotu, fosforu i potasu do grupy składników pokarmowych decydujących o ilości oraz jakości plonów roślin uprawnych. Rola siarki w żywieniu roślin zyskała na znaczeniu zwłaszcza w ciągu ostatnich kilku lat, kiedy to w większości krajów europejskich, w tym również w Polsce stwierdzono deficyt tego składnika w produkcji roślinnej. Związane to było przede wszystkim ze spadkiem emisji związków siarki do atmosfery oraz zmniejszeniem ilości tego składnika wprowadzanego do gleby z nawozami mineralnymi i naturalnymi. Funkcje jakie pełni ten pierwiastek oraz pogłębiający się deficyt tego składnika w środowisku wzrostu roślin wskazują, że siarka obok innych składników pokarmowych powinna być uwzględniana przy ustalaniu potrzeb nawozowych roślin uprawnych.

Słowa kluczowe: źródła siarki, siarka w roślinie, wielkość plonu, jakość plonu, siarka jako składnik deficytowy

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Małgorzata HAWROT-PAW[1]

ACTIVITY OF DEHYDROGENASES IN SOIL CONTAMINATED WITH DIESEL FUEL AND SUBJECTED TO BIOREMEDIATION PROCESS

AKTYWNOŚĆ DEHYDROGENAZ W GLEBIE ZANIECZYSZCZONEJ OLEJEM NAPĘDOWYM I PODDAWANEJ PROCESOWI BIOREMEDIACJI

Abstract: The carried out study referred to evaluation of the activity of dehydrogenases in soil that was contaminated with diesel fuel (5 % w/w). In addition, the influence of modifications used in the process of biodegradation of oil pollutions (agrotechnical measures, biostimulation, bioaugmentation) was evaluated. The experiment was made with *in situ* and *ex situ* methods. It was found that diesel fuel stimulated the activity of dehydrogenases. Also a highly significant effect of applied remediation measures was demonstrated.

Keywords: dehydrogenases, diesel fuel, soil

Petroleum hydrocarbons that get into environment cause in it a number of unfavourable changes. Changes in qualitative and quantitative composition of microorganisms and their activity are a sensitive indicator of the presence of pollutions of that type [1–5]. Many authors point at an important role that can be also played by enzymatic activity, including the activity of dehydrogenases [6–8]. Dehydrogenases, apart from oxygenases, participate in biological oxidation of organic compounds, thus their activity in contaminated soils should increase. However, the response of these enzymes to the presence of petroleum hydrocarbons in environment is not simple, since one can observe both stimulation [9, 10] and inhibition of the activity of dehydrogenases [11, 12] with the concentration of xenobiotic having a significant effect on the response observed [13]. The presented study aimed at evaluation of changes in the activity of dehydrogenases under the influence of diesel fuel and treatments used during remediation of contaminated soil made with *in situ* and *ex situ* methods.

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[1] Department of Microbiology and Environmental Biotechnology, West Pomeranian University of Technology, ul. J. Słowackiego 17, 71–434 Szczecin, tel. +48 91 44 96 423, email: Malgorzata.Hawrot-Paw@zut.edu.pl

Materials and methods

Bio-pile experiment (*ex situ* method) was carried out in a vegetation house of the University of Agriculture in Szczecin. In total, 4 piles were prepared, each being a single object: 1) K – control soil, uncontaminated and non-modified, 2) 0 – contaminated soil, non-modified by treatments, 3) I – contaminated soil, nutrient-supplemented and mixed, and 4) II – contaminated soil, modified by nutrient supplementation, mixing and inoculation with a mixture of bacteria cultures isolated from environments polluted with petroleum hydrocarbons – strains, definite as BS 101, BS 126 and BS 135, were described earlier by Nowak and Hawrot [14]. Diesel fuel was introduced into the soil at the concentration of 5 % (w/w). The concrete floor under piles was lined with foil coverings. As the need arose, the pile soil was protected against unfavourable climatic conditions by means of foil coverings. Soil moisture was kept a level of 20 % WHC. Fertilisation was used twice – at the beginning of experiment and after three months – the applied fertiliser doses corresponded to 500 kg N · ha^{-1} (twice, 250 kg N · ha^{-1} each), 120 kg P_2O_5 · ha^{-1} (once), 300 kg K_2O · ha^{-1} (twice, 150 kg K_2O · ha^{-1} each), when converted to 15 cm soil layer. The mixing in respective piles was made every second week. Every 30 days, collective soil samples were collected from a depth of 0–15 cm. In case of object 0, the soil samples were also collected from a depth of 15–30 cm and averaged with the sample from a depth 0–15 cm.

Field experiment (*in situ* method) was set up in the form of microplots with the method of completely randomised blocks in 4 replications. The microcosm were formed, corresponding to bio-pile experiment variants (K, 0, I, II). Diesel fuel was introduced into the soil at the concentration of 5 % (w/w – in count on layer 15 cm depth of plot 1×1 m size). The nutrient supplementation treatment within microcosm I and II was carried out at the beginning of experiment and after 3 months, with application of nitrogen supplementation (100 kg N · ha^{-1}), phosphorus supplementation (80 kg P_2O_5 · ha^{-1}) and potassium supplementation (100 kg K_2O · ha^{-1}). The mixing (by delving) was made every 14 days. The soil was kept under fallow to eliminate the effect of plants of biodegradation efficiency. Every 30 days, a collective soil sample was collected weighing 0.5 kg from a depth of 0–15 cm of each microcosm.

The activity of dehydrogenases in soil was determined by the method according to Malkomes [15]. Measurements were made with a wavelength of λ = 540 nm using a Perkin Elmer UV/VIS Lambda Bio spectrophotometer. Results are given as converted to μg TPF · g^{-1} · dm · $4h^{-1}$. The experiment was carried out for 150 days. The obtained results were subjected to statistical analysis using analysis of variance. Within the analysis of variance in the field experiment, effects were combined with error, which allowed for taking into consideration the block variation.

Results

The activity of dehydrogenases determined at the beginning of experiment with bio-piles amounted to 82 μg TPF. In the control pile, it underwent small fluctuations in range 74–125 μg TPF. After soil contamination with diesel fuel, enzymatic activity clearly increased in all piles, in particular in the third measurement time. In that time, lowest values were recorded in pile 0 (222 μg TPF), while the largest ones in the pile inoculated with a mixture of bacteria cultures (549 μg TPF). In next times, this enzymatic activity was gradually smaller and smaller in all piles. After 150 days of incubation, the values observed in pile 0–146 μg TPF, and in pile I and II – 222 μg TPF and 264 μg TPF, constituted respectively 198, 301 and 359 % when compared with the control (Fig. 1A).

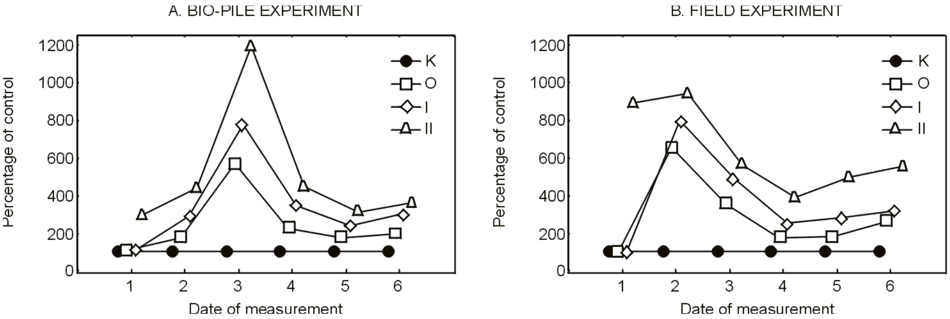

Fig. 1. Effect of soil contamination with diesel fuel in 5 % concentration and treatments used in biodegradation on the activity of dehydrogenases expressed as control percent

In the field experiment, the enzymatic activity determined at the beginning amounted to 26 μg TPF. In the control object this activity increased over 3 times after the third measurement time, to 82 μg TPF, whereupon decreased gradually to a level of 48 μg TPF at the end of experiment. In the soil contaminated with diesel fuel, the activity of dehydrogenases clearly increased. The largest activity in relation to the control was observed after 30 days of incubation, ranging from 656 % in object 0 to 940 % in object II (Fig. 1B). In next days, this activity gradually decreased. After 150 days of incubation, a value of 124 μg TPF was recorded in non-modified object, 150 μg TPF in fertilised and mixed object and 260 μg TPF in inoculated object. During the experiment, the lowest activity was observed in object 0–122 μg TPF, whereas the largest one in object II – 537 μg TPF.

Table 1

Results of statistical analysis for the activity of dehydrogenases in soil in the bio-pile experiment

Factor	Number of independent variables	Mean square sum.	Number of independent variables for error	Mean square sum for error	F value	P value
1	3	445.1544	48	0.467564	952.071	0.00*
2	5	232.0776	48	0.467564	496.354	0.00*
1 × 2	15	26.5867	48	0.467564	56.862	0.00*

Factors: 1 – bioremediation treatment, 2 – measurement period
* = a significant effect of a factor (at $P < 0.05$)

Table 2

Results of statistical analysis for the activity of dehydrogenases in soil in the field experiment

Variation source	Sum of squares	Degrees of freedom	Mean of squares	F value	P value
Blocks	0.89961	3	0.299869		
1	5149.585	3	1716.529	1301.347	0.00*
2	1645.506	5	329.101	249.501	0.00*
1 × 2	463.6986	15	30.91324	23.436	0.00*
Error	91.0137	69	1.31904		

Factors: 1 – bioremediation treatment, 2 – measurement period
* = a significant effect of a factor (at $P < 0.05$)

Discussion and conclusions

Biodegradation efficiency depends on the activity of microorganisms which participate in biological decomposition of petroleum products. The measure of their activity can be the enzymatic activity [16, 17]. Dehydrogenase activity has been suggested as suitable sensitive parameter to organic pollutant contamination among several biological indicators [18]. In our study after introduction of diesel fuel into soil, an increase in the activity of dehydrogenases was found. In the bio-pile soil, the enzymatic activity was higher that in the soil of field experiment. Similar situation was found in fertilised and mixed objects, whereas after soil inoculation a clearly higher activity of dehydrogenases was observed in the bio-pile, maybe the selected bacteria strains introduced into soil brought about an increase in total number of microorganisms, which in turn affected the increase of respiratory activity, the measure of which is enzymatic activity. Stimulation the microbial activity after addition of nutrient (nitrogen and phosphorus) was observed by Bento et al [19] and Lee et al [20]. Bento et al [19] found the highest dehydrogenase activity after bioaugmentation too. Hawrot et al [10] observed in the study carried out under laboratory conditions that both diesel fuel and modifications applied during their experiment (biostimulation and bioaugmentation) stimulated enzymatic activity, however after 90 days of incubation the values were at a higher level in the inoculated object than in the control one. The study carried out by Margesin and Schinner [9] confirm an increase in the activity of dehydrogenases, in particular in the soil samples into which bacteria inoculate was introduced. Also other authors [21, 22] demonstrated a clearly stimulating effect of diesel fuel. Different results are reported by Claassens et al [11] and Dawson et al [12]. They observed decrease of dehydrogenases activity in soil after petroleum hydrocarbon contamination compared with the uncontaminated soil.

In our study maximum activity of dehydrogenases was found after 60 days of incubation in the bio-pile experiment and after 30 days in the field experiment. Riffaldi et al [23] have recently shown much higher activity in uncontaminated samples than that of the contaminated soil until the 20th day of the experiment, but since the 35th day he observed increased, probably connected with end of initial adaptation phase microorganisms able to utilize hydrocarbons as a carbon source.

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AKTYWNOŚĆ DEHYDROGENAZ W GLEBIE ZANIECZYSZCZONEJ OLEJEM NAPĘDOWYM I PODDAWANEJ PROCESOWI BIOREMEDIACJI

Katedra Mikrobiologii i Biotechnologii Środowiska,
Zachodniopomorski Uniwersytet Technologiczny

Abstrakt: Przeprowadzone badania dotyczyły oceny aktywności dehydrogenaz w glebie, którą zanieczyszczono olejem napędowym. Dodatkowo oceniano wpływ modyfikacji stosowanych w procesie biodegradacji skażeń substancjami ropopochodnymi (zabiegi agrotechniczne, biostymulacja, bioaugmentacja). Doświadczenia prowadzono metodą *in situ* oraz *ex situ*. Stwierdzono, że olej napędowy stymulował aktywność dehydrogenaz. Ponadto wykazano statystycznie wysoce istotny wpływ stosowanych zabiegów remediacyjnych.

Słowa kluczowe: dehydrogenazy, olej napędowy, gleba

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Dorota KALEMBASA[1] and Elżbieta MALINOWSKA[1]

INFLUENCE OF MINERAL FERTILIZATION ON TOTAL CONTENTS OF Co, Li, AND Ti IN BIOMASS OF FIVE *MISCANTHUS* GENOTYPES

WPŁYW NAWOŻENIA MINERALNEGO NA ZAWARTOŚĆ OGÓLNĄ Co, Li AND Ti W BIOMASIE PIĘCIU GENOTYPÓW TRAWY *MISCANTHUS*

Abstract: The study involved five different genotypes of *Miscanthus* grass (ecotypes of different origin), ie two diploid: No. 1 and No. 19, as well as three triploid: No. 53, No. 63, and POL. After the second year of *Miscanthus* cultivation, total contents of Co, Li, and Ti were determined in a plant material, including leaves, stems, roots, and rhizomes. The mineral fertilization differentiated the contents of studied elements in majority of *Miscanthus* parts. The highest concentrations (mean for a fertilization) of Co and Ti were determined in roots and Li in rhizomes, while the lowest levels of Co, Li, and Ti were recorded in stems of tested grass. Greater Co accumulation for diploid (except from stems), Li for triploid, and Ti for triploid genotypes (except from leaves) was recorded.

Keywords: *Miscanthus* grass, biomass, cobalt, lithium, titanium, fertilization

Miscanthus is a gigantic grass species belonging to *Miscanthus* genus. That plant began to be used in 80s of the twentieth century [1]. At present, it is a valuable material for various industrial branches, namely for energetic purposes [2–4]. *Miscanthus* growth and development is affected by many factors: among others, morphological traits (rhizome size and genotype), agrotechnics, and fertilization [5].

The study aimed at evaluating the mineral fertilization influence and the genotype on cobalt, lithium, and titanium contents in leaves, stems, roots, and rhizomes of five *Miscanthus* genotypes at the second cultivation year.

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[1] Department of Soil Science and Agricultural Chemistry, University of Podlasie in Siedlce, ul. B. Prusa 14, 08–110 Siedlce, tel. 025 643 13 52, email: kalembasa@ap.siedlce.pl

Materials and methods

The field experiment was set in autumn 2000 under soil and climatic conditions of middle-eastern Poland on the soil of loamy sand granulometric composition (according to PN-R-04033), with $pH_{KCl} = 6.73$. The organic carbon content was 37.4 g · kg^{-1}, and studied elements [mg · kg^{-1} of soil]: Co – 4.62, Li – 1.70, and Ti – 49.42. Five genotypes of *Miscanthus* were chosen: 2 diploid (2x) representing *Miscanthus sinensis* species (clone No. 1 from *Hybriden* grass group and clone No. 19 – German form "Goliath" – MGo); 3 triploid (3×) being the *Miscanthus sinensis* x *gigantheus* hybrids (clone No. 53 from Germany, clone No. 63 from Denmark, and clone POL from Poland). Rhizomes achieved from the rhizome reproduction were set on 1.5 m^2 area in three replications in completely randomized pattern. The experiment included two fertilization objects:

– control (with no fertilization);

– mineral fertilization [kg · ha^{-1}]: N_{60} P_{50} K_{100} in a form of ammonium nitrate, triple superphosphate, and potassium sulfate applied once a year before vegetation beginning.

Total contents of cobalt, lithium, and titanium were determined in the grass harvested in winter 2002 and divided into leaves, rhizomes, stems, and roots. The plant material was ground till 0.25 mm of particle diameter, aliquots of 1 g were weighed into the stoneware crucible, and then combusted in the muffle furnace at 450 ^{o}C for 15 hours. Portions of 10 cm^3 diluted HCl (1:1) were added into crucibles and evaporated till dryness on a sandy bath to decompose carbonates and separate silicates. After adding 5 cm^3 10 % HCl, the crucible content was transferred through hard filter paper to the measure flask and adjusted volume to 100 cm^3 with distilled water. Total contents of Co, Li, and Ti in plant material were determined by means of ICP-EAS technique.

Achieved results were statistically processed; differences between mean values for studied factors were estimated applying variance analysis (helped with FR Analvar 4.1 software), and in the case of difference significance, $LSD_{0.05}$ values were calculated according to Tukey's test.

Results and discussion

Cobalt concentration in analyzed plant material varied (Table 1). Its highest amounts were found in roots of diploid (1.45 mg · kg^{-1}) and triploid genotypes (1.35 mg · kg^{-1}); while the lowest levels in stems (0.183 and 0.224 mg · kg^{-1}, respectively). Kalembasa et al [6] and Jeżowski et al [7] reported similar dependence of other elements accumulation – ie potassium, copper, nickel, and chromium – in particular parts of *Miscanthus* grass. NPK fertilization did not make significant differences in cobalt content in studied parts of diploid genotypes, whereas considerable differences were observed for its levels in leaves, stems, and roots of triploid clones. Increase of cobalt concentration due to fertilization was recorded in leaves and stems of studied grass: more for triploid genotypes as well as in roots and rhizomes of only triploid genotypes. Studies revealed that leaves, rhizomes, and roots of diploid clones were characterized by higher cobalt accumulation as compared to triploid ones. Contents of cobalt [mg · kg^{-1}] at analyzed

Table1

Total content of cobalt [mg · kg^{-1} d.m.] in above- and underground parts of *Miscanthus*

Genotypes	Leaves			Stems			Rhizomes			Roots		
	0	NPK	mean	0	NPK	mean	0	NPK	mean	0	NPK	mean
	diploid genotypes											
No. 1	0.233	0.136	0.184	0.187	0.202	0.195	0.372	0.383	0.377	1.63	1.13	1.38
No. 19	0.200	0.526	0.363	0.098	0.245	0.172	0.245	0.189	0.217	1.53	1.53	1.53
Mean for diploid genotypes	0.217	0.331	0.274	0.143	0.224	0.183	0.309	0.286	0.297	1.58	1.33	1.45
Changes in cobalt content in analysed parts of plant	0.114			0.081			–0.023			–0.250		
LSD$_{0.05}$ for: A – fertilization B – genotypes A/B – interaction B/A – interaction	 n.s. 0.171 0.242 0.242			 n.s. n.s. n.s. n.s.			 n.s. 0.141 n.s. n.s.			 n.s. n.s. n.s. n.s.		
	triploid genotypes											
No. 53	0.203	0.247	0.225	0.099	0.247	0.173	0.227	0.214	0.220	1.06	1.68	1.37
No. 63	0.153	0.296	0.225	0.110	0.234	0.172	0.207	0.194	0.201	1.29	1.30	1.29
POL	0.142	0.456	0.299	0.197	0.456	0.327	0.384	0.430	0.407	1.44	1.36	1.40
Mean for triploid genotypes	0.166	0.333	0.249	0.135	0.312	0.224	0.273	0.351	0.276	1.26	1.45	1.35
Changes in cobalt content in analysed parts of plant	0.167			0.177			0.078			0.190		
LSD$_{0.05}$ for: A – fertilization B – genotypes A/B – interaction B/A – interaction	 0.093 n.s. n.s. n.s.			 0.082 0.122 n.s. n.s.			 n.s. 0.143 n.s. n.s.			 0.165 n.s. 0.286 0.351		

n.s. – non significant difference

Miscanthus grass can be lined up in a form of the following sequence (mean for the fertilization):

– roots: No. 19 (1.53) > POL (1.40) > No. 1 (1.38) > No. 53 (1.37) > No. 63 (1.29);

– rhizomes: POL (0.407) > No. 1 (0.377) > No. 53 (0.220) > No. 19 (0.217) > No. 63 (0.210);

– leaves: No. 19 (0.363) > POL (0.299) > No. 53 (0.225) = No. 63 (0.225) > No. 1 (0.184);

– stems: POL (0.327) > No. 1 (0.195) > No. 53 (0.173) > No. 63 (0.172) = No. 19 (0.172).

The highest lithium levels were found in *Miscanthus* underground parts, namely in rhizomes of all studied genotypes (Table 2). Rhizomes of diploid genotypes contained (mean for fertilization) 26.19 mg Li · kg^{-1}, while triploid ones 34.21 mg Li · kg^{-1}. Diploid genotypes were characterized by lower average lithium accumulation than triploid ones for all analyzed parts of the grass. Mineral fertilization affected the decrease of the element concentration in leaves, stems, and roots of diploid clones, as well as leaves and rhizomes of triploid genotypes. Lithium contents [mg · kg^{-1}] in studied parts of *Miscanthus* can be lined up in the following sequences (mean for fertilization):

– rhizomes: POL (42.22) > No. 63 (33.15) > No. 19 (28.28) > No. 53 (27.25) > No. 1 (24.11);

– roots: POL (19.81) > No. 53 (16.17) > No. 63 (15.77) > No. 19 (13.55) > No. 1 (6.78);

– leaves: POL (16.54) > No. 19 (13.17) > No. 63 (11.45) > No. 53 (7.42) > No. 1 (7.20);

– stems: No. 63 (17.77) > No. 53 (12.49) > POL (9.71) > No. 19 (9.56) > No. 1 (5.63).

The poorest lithium bioaccumulation was recorded for diploid clone No. 1, while the richest for triploid clone POL (except from the stems).

Mineral NPK fertilization significantly differentiated titanium content in studied parts of tested plant (Table 3). Due to the fertilization, total concentration of titanium increase, except from stems of diploid genotypes (–0.390 mg · kg^{-1}) and leaves of triploid clones (–0.590 mg · kg^{-1}). Underground organs (roots and rhizomes) were characterized by almost 20-fold higher concentration of the element than aboveground parts (leaves and stems). Total contents of titanium (mg · kg^{-1}) in under- and aboveground parts of *Miscanthus* can be lined up in following sequences (mean for fertilization):

– roots: POL (75.16) > No. 53 (70.75) > No. 63 (63.86) > No. 19 (55.26) > No. 1 (52.35);

– rhizomes: No. 63 (34.45) > No. 53 (34.09) > No. 1 (31.34) > No. 19 (26.60) > POL (24.44);

– leaves: No. 19 (4.05) > No. 1 (3.47) > POL (2.79) > No. 63 (2.58) > No. 53 (2.50);

– stems: No. 53 (2.62) > POL (2.46) > No. 63 (2.22) > No. 19 (1.79) > No. 1 (0.853).

Underground parts of five studied genotypes of *Miscanthus* genus (rhizomes and roots) contained more cobalt, lithium, and titanium than aboveground organs (leaves

Table 2

Total content of lithium [mg · kg^{-1} d.m.] in above- and underground parts of *Miscanthus*

Genotypes	Leaves			Stems			Rhizomes			Roots		
	0	NPK	mean	0	NPK	mean	0	NPK	mean	0	NPK	mean
	diploid genotypes											
No. 1	8.27	6.12	7.20	6.60	4.67	5.63	15.23	32.98	24.11	6.28	7.27	6.78
No. 19	15.80	3.66	13.17	10.74	8.42	9.56	26.73	29.82	28.28	14.22	12.88	13.55
Mean for diploid genotypes	12.04	4.89	10.18	8.67	6.55	7.60	20.98	31.40	26.19	10.25	10.08	10.16
Changes in lithium content in analysed parts of plant	–7.15			–2.12			10.42			–0.170		
$LSD_{0.05}$ for: A – fertilization B – genotypes A/B – interaction B/A – interaction	 3.37 3.37 4.76 4.76			 10.03 10.03 n.s. n.s.			 8.02 n.s. n.s. n.s.			 n.s. 2.81 n.s. n.s.		
triploid genotypes												
No. 53	8.48	6.35	7.42	7.45	17.54	12.49	30.25	24.24	27.25	15.16	17.19	16.17
No. 63	18.58	4.32	11.45	4.50	31.04	17.77	40.33	25.98	33.15	18.98	12.57	15.77
POL	25.46	7.63	16.54	1.49	17.92	9.71	59.17	25.28	42.22	17.58	22.09	19.81
Mean for triploid genotypes	17.51	6.10	11.80	4.48	22.17	13.32	43.25	25.17	34.21	17.22	17.28	17.25
Changes in lithium content in analysed parts of plant	–11.41			17.69			–18.08			0.060		
$LSD_{0.05}$ for: A – fertilization B – genotypes A/B – interaction B/A – interaction	 0.686 1.03 1.89 1.46			 3.95 5.92 6.84 8.37			 10.87 n.s. n.s. n.s.			 n.s. 3.08 3.56 4.35		

n.s. – non significant difference

Table 3

Total content of titanium [mg · kg^{-1} d.m.] in above- and underground parts of *Miscanthus*

Genotypes	Leaves			Stems			Rhizomes			Roots		
	0	NPK	mean	0	NPK	mean	0	NPK	mean	0	NPK	mean
	diploid genotypes											
No. 1	3.11	3.83	3.47	0.829	0.878	0.853	24.98	37.69	31.34	45.46	59.23	52.35
No. 19	3.75	4.35	4.05	2.20	1.37	1.79	25.03	28.18	26.60	17.71	92.81	55.26
Mean for diploid genotypes	3.43	4.09	3.76	1.51	1.12	1.32	25.01	32.94	28.97	31.59	76.02	53.80
Changes in titanium content in analysed parts of plant	0.660			–0.390			7.93			44.43		
LSD$_{0.05}$ for: A – fertilization B – genotypes A/B – interaction B/A – interaction	 0.136 0.136 n.s. n.s.			 0.067 0.067 0.095 0.095			 1.75 1.75 2.48 2.48			 4.11 n.s. 5.82 5.82		
triploid genotypes												
No. 53	2.69	2.31	2.50	2.71	2.52	2.62	33.14	35.14	34.09	52.11	89.39	70.75
No. 63	3.56	1.80	2.58	1.84	2.60	2.22	32.14	36.76	34.45	44.06	83.66	63.86
POL	2.61	2.97	2.79	1.15	3.62	2.46	21.29	27.59	24.44	69.73	80.58	75.16
Mean for triploid genotypes	2.95	2.36	2.62	1.90	2.91	2.43	28.86	33.15	30.99	55.30	84.54	69.92
Changes in titanium content in analysed parts of plant	–0.590			1.01			4.29			29.24		
LSD$_{0.05}$ for: A – fertilization B – genotypes A/B – interaction B/A – interaction	 0.199 n.s. 0.345 0.422			 0.319 n.s. 0.552 0.676			 3.63 5.44 n.s. n.s.			 10.27 n.s. n.s. n.s.		

n.s. – non significant difference

and stems). It probably resulted from the autumn translocation of nutrients towards underground rhizomes that determine the sensitivity to low temperatures and wintering [8]. Accumulation of elements, namely toxic, in roots is very positive phenomenon at energetic utilization of plants.

Conclusions

1. Mineral fertilization of *Miscanthus* genus grass differentiated contents of cobalt, lithium, and titanium in majority of analyzed above- and underground organs of the plant.
2. Much more cobalt was found in roots, while lithium and titanium in rhizomes than in stems and leaves of studied grass.
3. Higher cobalt accumulation for diploid (except from stems), lithium for triploid, and titanium for triploid genotypes (except from leaves) was recorded.

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WPŁYW NAWOŻENIA MINERALNEGO NA ZAWARTOŚĆ OGÓLNĄ Co, Li AND Ti W BIOMASIE PIĘCIU GENOTYPÓW TRAWY *MISCANTHUS*

Katedra Gleboznawstwa i Chemii Rolniczej, Akademia Podlaska w Siedlcach

Abstrakt: W badaniach wykorzystano pięć różnych genotypów trawy *Miscanthus* (ekotypów różnego pochodzenia), tj. dwa diploidalne: nr 1 i nr 19 oraz trzy triploidalne: nr 53, 63 i POL. Po zakończeniu II roku uprawy miskanta zbadano ogólną zawartość Co, Li i Ti w materiale roślinnym, obejmującym liście, łodygi, korzenie i rizomy. Nawożenie mineralne zróżnicowało zawartość analizowanych pierwiastków w większości badanych części miskanta. Największą zawartość (średnia z nawożenia) Co i Ti stwierdzono w korzeniach, Li w rhizomach, natomiast najmniejszą zawartość Co, Li i Ti oznaczono w łodygach badanej trawy. Zanotowano większą kumulację Co dla genotypów diploidalnych (z wyjątkiem łodyg), Li dla triploidalnych, Ti dla triploidalnych (za wyjątkiem liści).

Słowa kluczowe: trawa *Miscanthus*, biomasa, kobalt, lit, tytan, nawożenie

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Beata KUZIEMSKA[1] and Stanisław KALEMBASA[1]

INFLUENCE OF SOIL CONTAMINATION WITH NICKEL AT VARIOUS ACIDITY ON A BASE OF CALCIUM AND MANGANESE CONTENTS IN BEANS

OCENA WPŁYWU ZANIECZYSZCZENIA GLEBY NIKLEM PRZY ZRÓŻNICOWANYM JEJ ODCZYNIE NA PODSTAWIE ZAWARTOŚCI WAPNIA I MANGANU W FASOLI

Abstract: The four-year pot experiment dealt with the influence of soil contamination with nickel (0, 50, 100, and 150 mg Ni · kg^{-1} soil) and liming (without or with liming according to 0.5, 1, and 1.5 Hh soil) on calcium and manganese contents in particular parts of Aura cv. bean plants (roots, stems, leaves, siliques, and seeds). Concentrations of Ca and Mn in plant material were determined by means of ICP-AES technique after previous combustion in muffle furnace at 450 ^{o}C and dissolving the ash in 10 % HCl. Numerical results were statistically processed applying variance analysis and using F-Fisher–Snedecor's test (F.R.Anal. ver. 4.1. software), while LSD values were calculated with a help of Tukey's test. Soil contamination with nickel and liming did not differentiate mean calcium and manganese levels over study years in analyzed bean parts, except from seeds, for which liming caused the decrease of manganese concentration.

Keywords: bean, soil contamination with nickel, liming, calcium, manganese

In general, the industrial pollution contribute to stronger degradation of agricultural production area leading, among others, to accumulation of heavy metals in the soil. Due to that, most of metals are involved into the trophic chain – soil → plants → animals → people with opportunity to accumulate in human's organisms. Nickel is a heavy metal that, in small amounts, is necessary to grow and development of living organisms, while at excess, it is toxic. Nickel concentration in the soil environment may greatly increase under influence of anthropogenic factors, which causes negative ecological effects. Nickel contamination of ecosystems is a threat mainly for plants that are first link of the nutrition chain [1]. Excessive nickel amounts at plants reduce their photosynthesis and transpiration. Nickel also disturbs the cation-anion balance within green parts of plants [2]. The Ni^{2+} toxicity is considerably affected by other metals [3]. Nickel takes part in

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[1] Department of Soil Science and Agricultural Chemistry, University of Podlasie, ul. B. Prusa 14, 08–110 Siedlce, tel./ fax: 025 643 12 87; email: kalembasa@ap.siedlce.pl

antagonistic interactions with Ca, K, Mg and Mn, in possible antagonism with Co, whereas with Cu and Zn, nickel can be present both in antagonistic and synergistic systems [4].

The aim of present study was to evaluate the influence of soil contamination with nickel at various acidity on calcium and manganese contents in bean plants.

Material and methods

The four-year pot experiment was carried out in the greenhouse owned by University of Podlasie in Siedlce, in completely randomized pattern. Following factors were examined: I – soil contamination with nickel (0, 50, 100, 150 mg Ni $\cdot$ kg^{-1} soil – nickel in the form of $NiSO_4 \cdot 7H_2O$ solution applied at the beginning of June); II – liming (without or with liming according to 0.5, 1.0, and 1.5 Hh soil – in the form of $CaCO_3$ applied at the beginning of May).

Pots were not tilled for the first season, maintaining only the moisture content at the level of 60 % field water capacity, then dwarf bean (Aura cv.) was cultivated for four subsequent years. Once at each vegetation period, before sowing, following mineral fertilization was applied: N – 0.17 g $\cdot$ kg^{-1} soil in the form of NH_4NO_3 (34 % N); P – 0.053 g $\cdot$ kg^{-1} soil in the form of $Ca(H_2PO_4)_2$ (19 %); K – 0.17 g $\cdot$ kg^{-1} soil in the form of KCl (40 % K). The soil material used for the experiments was collected from the humus layer of typical podzolic soils that had following features: pH_{KCl} – 5.49; $C_{org.}$ – 6.5 g $\cdot$ kg^{-1} soil; $N_{tot.}$ – 0.61 g $\cdot$ kg^{-1} soil; P and available K (mg $\cdot$ kg^{-1} soil) – 71 and 110, respectively; total nickel content: 10.1 mg $\cdot$ kg^{-1}. Every year after harvest, samples were divided into particular plant fragments (roots, stems, leaves, siliques, seeds) and dried to estimate the dry matter content. Concentrations of Ca and Mn in plant material were determined by means of ICP-AES technique after combustion in muffle furnace at 450 ^{o}C and dissolving the ash in 10 % HCl [5]. Results were statistically processed by means of variance analysis applying F-Fisher–Snedecor's tests and using F.R. Anal. Ver. 4.1. software, while $LSD_{0.05}$ values were calculated according to Tukey's test. To find the interactions between studied traits, also linear correlation analysis was presented in the paper.

Results and discussion

Under the experimental conditions, average calcium content in particular bean parts calculated on a base of four-year results (Table 1) did not significantly change due to soil contamination with nickel and liming.

However, these results are not consistent with earlier achieved ones [6], that revealed that usually more calcium can be found in plants grown on limed as compared with not limed soils. Such discrepancy may be associated with the fact that liming was made five years before, hence its effects became negligible.

Mean calcium content for the whole bean plant (Table 1) was within the range between 17.8 and 20.8 g Ca $\cdot$ kg^{-1} d.m., which was the highest value in the case of plants grown on soils contaminated with nickel to the highest extent and limed with the calcium fertilizer according to 1.5 Hh soil. Content of calcium in particular bean plant fragments can be lined up in the following sequence: leaves > stems > roots > siliques > seeds.

Table 1

Mn content in bean [mg · kg^{-1} d.m.] (mean for four years of experiment)

Objects		Parts of plant					
Doses of nickel [mg · kg^{-1} soil]	Liming according to Hh	Roots	Bean stalks	Leaves	Stripped pods	Seed	Mean for plant
0	0	26.2	14.1	84.3	19.1	12.8	31.3
	0.5	31.5	13.3	81.0	18.1	10.6	30.9
	1.0	32.3	15.1	91.2	20.0	11.7	34.1
	1.5	31.1	15.0	75.3	16.8	12.2	30.1
50	0	27.1	16.3	112.0	20.3	12.9	37.7
	0.5	32.8	16.9	95.9	19.1	11.1	35.2
	1.0	23.7	14.9	92.8	16.0	10.5	31.6
	1.5	29.2	14.6	75.0	15.8	10.7	29.1
100	0	26.9	17.2	98.6	18.4	13.6	34.9
	0.5	31.8	17.0	85.0	17.8	10.7	32.5
	1.0	30.0	14.6	72.5	16.4	10.3	28.8
	1.5	25.7	14.0	87.4	20.0	11.0	31.6
150	0	30.2	12.2	82.7	20.7	10.5	31.3
	0.5	25.0	16.7	75.8	17.4	10.5	29.1
	1.0	30.8	13.6	90.4	18.2	11.2	32.8
	1.5	28.7	12.6	67.7	18.1	10.9	27.6
Mean for doses of nickel	0	30.3	14.4	83.0	18.5	11.8	31.6
	50	28.2	15.7	93.9	17.8	11.3	33.4
	100	28.6	15.7	85.9	18.2	11.4	32.0
	150	28.7	13.8	79.2	18.6	10.8	30.2
Mean for liming	0	27.6	15.0	94.4	19.6	12.5	33.8
	0.5	30.3	16.0	84.4	18.1	10.7	31.9
	1.0	29.2	14.6	86.7	17.7	10.9	31.8
	1.5	28.7	14.0	76.4	17.7	11.2	29.6
Mean in experiment		29.0	14.9	85.5	18.3	11.3	31.8

	Roots	Bean stalks	Leaves	Stripped pods	Seed
LSD$_{0.05}$ for:					
doses of nickel	n.i.	n.i.	n.i.	n.i.	0.623
liming	n.i.	n.i.	n.i.	n.i.	0.623
interaction: doses of nickel x liming	n.i.	n.i.	n.i.	n.i.	1.246

Mean manganese concentration in analyzed parts of the bean plants calculated on a base of four-year results (Table 2) did not considerably vary due to soil contamination with nickel and liming, except from seeds, for which following dependence was recorded: fragments from plants grown on nickel-polluted and not-limed soils were characterized by the highest manganese contents.

Table 2

Ca content in bean [g · kg^{-1} d.m.] (mean for four years of experiment)

Objects		Parts of plant					
Doses of nickel [mg · kg^{-1} soil]	Liming according to Hh	Roots	Bean stalks	Leaves	Stripped pods	Seed	Mean for plant
0	0	9.33	17.6	660.5	7.66	1.61	19.3
	0.5	8.04	16.7	54.9	8.74	1.42	18.0
	1.0	9.13	19.7	57.8	9.03	1.40	19.4
	1.5	9.30	20.9	56.7	7.39	1.44	18.9
50	0	9.39	18.3	54.0	8.53	1.54	18.4
	0.5	9.48	19.7	49.5	8.88	1.49	17.8
	1.0	8.84	20.0	49.8	8.83	1.54	17.8
	1.5	10.2	19.3	56.0	7.68	1.38	18.9
100	0	7.27	18.9	57.9	9.13	1.55	19.0
	0.5	10.1	20.7	59.5	9.26	1.39	20.2
	1.0	8.92	20.2	52.6	8.72	1.42	18.4
	1.5	10.9	19.1	56.4	8.44	1.33	19.2
150	0	9.41	17.8	61.9	9.35	1.48	20.0
	0.5	10.1	19.7	53.6	8.54	1.37	18.7
	1.0	9.41	20.5	56.3	8.74	1.50	19.3
	1.5	9.17	18.6	60.9	8.75	1.32	19.7
Mean for doses of nickel	0	8.95	18.7	57.5	8.20	1.47	18.9
	50	9.48	19.3	52.3	8.48	1.49	18.2
	100	9.30	19.7	56.6	8.89	1.42	19.2
	150	9.52	19.1	57.5	8.84	1.41	19.3
Mean for liming	0	8.85	18.1	58.6	8.67	1.55	19.2
	0.5	9.43	19.2	54.4	8.85	1.42	18.7
	1.0	9.08	20.1	54.1	8.83	1.46	18.7
	1.5	9.89	19.5	57.5	8.06	1.37	19.3
Mean in experiment		9.31	19.2	56.1	8.60	1.45	18.9

	Roots	Bean stalks	Leaves	Stripped pods	Seed
LSD$_{0.05}$ for:					
doses of nickel	n.i.	n.i.	n.i.	n.i.	n.i.
liming	n.i.	n.i.	n.i.	n.i.	n.i.
interaction: doses of nickel x liming	n.i.	n.i.	n.i.	n.i.	n.i.

Other authors reported [7–11] that solubility, therefore availability of most of metals, including manganese, decreased along with the pH increase. Here achieved results for bean seeds completely confirmed that observation.

Mean manganese content for the whole bean plant ranged within 27.6 to 37.7 mg Mn · kg^{-1} d.m., which was the highest at plants cultivated of soils contaminated with nickel to the lowest extent (50 mg Ni · kg^{-1} soil) and not limed. Concentration of manganese in particular fragments of tested plant can be lined up in the following sequence: leaves > roots > siliques > stems > seeds.

Statistical analysis revealed significant correlations between average value for experimental years vs. calcium and manganese contents in bean seeds ($r = 0.59^*$).

Both soil contamination with nickel and liming did not cause significant changes in calcium and manganese concentrations in analyzed bean plant fragments (except from seeds), which can be attributed to excessively long time from the agents introducing into the soil and their action disappearance. Here performed experiment did not confirm the antagonistic dependencies between nickel vs liming and manganese content, which was described in the literature [4].

Conclusions

1. Soil contamination with nickel did not significantly differentiate the mean value of calcium and manganese contents in analyzed parts of bean plants.
2. Applied liming did not differentiate the mean calcium concentration in analyzed parts of bean plants and it caused the decrease of mean manganese content in bean seeds with no differentiation of its level in other bean plant fragments.
3. Experiments did not confirm the antagonistic dependencies between nickel vs. calcium and manganese.

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OCENA WPŁYWU ZANIECZYSZCZENIA GLEBY NIKLEM PRZY ZRÓŻNICOWANYM JEJ ODCZYNIE NA PODSTAWIE ZAWARTOŚCI WAPNIA I MANGANU W FASOLI

Katedra Gleboznawstwa i Chemii Rolniczej, Akademia Podlaska w Siedlcach

Abstrakt: W czteroletnim doświadczeniu wazonowym badano wpływ zanieczyszczenia gleby niklem (0, 50, 100 i 150 mg Ni · kg^{-1} gleby) i wapnowania (bez wapnowania i wapnowanie wg 0,5; 1 i 1,5 Hh gleby) na zawartość wapnia i manganu w poszczególnych częściach fasoli (korzenie, łodygi, liście, łuszczyny i nasiona) odmiany Aura. Zawartość Ca i Mn w materiale roślinnym oznaczono metodą ICP-AES po wcześniejszej mineralizacji „na sucho” w piecu muflowym w temperaturze 450 °C i rozpuszczeniu popiołu w 10 % roztworze HCl. Wyniki badań opracowano statystycznie analizą wariancji z wykorzystaniem rozkładu F-Fishera–Snedecora wg programu F.R.Anal.var 4.1., a wartość NIR obliczono wg testu Tukey'a. Zanieczyszczenie gleby niklem i wapnowanie nie różnicowały średniej z lat badań zawartości wapnia i manganu w analizowanych częściach fasoli z wyjątkiem nasion, w przypadku których wapnowanie spowodowało zmniejszenie zawartości manganu.

Słowa kluczowe: fasola, zanieczyszczenie gleby niklem, wapnowanie, wapń, mangan

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Waldemar MARTYN[1]

CHEMICAL EVALUATION OF HAY FROM SELECTED TYPES OF GRASS WITH RESPECT TO ITS USABILITY FOR POWER ENGINEERING INDUSTRY

CHEMICZNA OCENA SIANA WYBRANYCH TRAW W KONTEKŚCIE ICH PRZYDATNOŚCI W ENERGETYCE

Abstract: The aim of the study was to evaluate the contents of alkaline elements in soil and hay obtained from grass with respect to the possibility of their use as a fuel in furnaces of power engineering industry. Two significantly different types of grass were used in the investigation: *Miscanthus sacchariflorus* and *Calamagrostis epigejos*. The experiment was started on typical for the northern part of the Lublin region podsolic soils that belong to quality class IVb, in the objects of Łęczyńska Energetyka in KWK Bogdanka. The plants were cultivated in conditions similar to these used during their production cultivation, but without the traditional mineral fertilization, which was replaced with post-sewage waters from the local, industrial, mechanical-biological sewage plant. The study revealed that both types of grass had useful properties for burning biomass, because they contained limited amounts of alkaline elements, however, there was a significant discrepancy in absorption of alkaline elements by both grasses.

Keywords: grass, hay, biomass, *Miscanthus sacchariflorus, Calamagrostis epigejos*, alkaline elements, post-sewage waters

Many authors have been claiming that grasses can be used practically as energy plants [1–7]. This fact is due to at least two reasons. Grasses are perennial plants and have constant growth during the vegetation period, results in high demand for water and nutrients. In favorable environmental conditions they provide high yield of biomass which can be harvested a few times during one vegetation period. The biomass of these plants subjected to rainfall for a long period of time improves its energy properties.

The other reason is economic in nature – with the decrease of the number of farm animals there is an excess of food that is not used by a herd and can be used for purposes other than consumption.

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[1] Faculty of Agricultural Sciences in Zamość, University of Life Sciences in Lublin, Institute of Natural Sciences and Mathematics, State Vocational Higher School in Zamość, Department of Protection and Management of Environment, ul. Szczebrzesla 102, 22–400 Zamość, email: waldemar@op.pl

The shape of the landscape where meadows and pastures are situated allows for their irrigation with flooding, and fertilization in the lowest places. Liquid sewage and pre-filtered post-sewage waters can be used for fertilization. This process is similar to filtering sewage in root sewage plants. Such kind of fertilization can be used practically because grass-like plants have coronal roots and by tightly covering soil surface create a natural barrier that protects the liquids from moving deeper into soil profile. During grass fertilization the contents and mutual co-relations between alkaline cations are taken into consideration as a criterion for creating proper growing conditions for grasses [8–10].

When assessing biomass that is used for energy purposes much attention is paid to the presence of at least a few elements, including alkaline elements. In many cases amounts and mutual corelations of these elements can be, at least partially, regulated by human.

In spite of a positive properties of biomass as a fuel and from the point of view of protection of environment, its combustion is not widespread because of some technical problems. The contents of silica and potassium significantly decrease the value of biomass as a fuel. High contents of alkaline elements causes slag to clot, which makes it difficult for the organic mass to move along the grates of the furnace [11, 12]. It is also believed, that potassium and alkaline elements influence the melting point of ash, which is an important energy property of a fuel [13, 14].

The aim of the study it was evaluation of the contents of alkaline elements in soil and hay obtained from grass with respect to their usability as a fuel in furnaces of professional power industry. Such study may provide reasons for using the investigated plants not only as a fuel, but also for bioremediation of soil environment, especially where there is an excess of biogenes.

Material and methods

Two significantly different types of grass were used in the study – *Miscanthus sacchariflorus* and *Calamagrostis epigejos*. The experiment was started with typical for the northern part of the Lublin region podsolic soils that belong to quality class IVb, in the objects of Łęczyńska Energetyka in KWK Bogdanka. The plants have been growing on plots which surface was 36 m^2. The presented results cover only the year 2007 – the third year of the experiment. The plants were cultivated in conditions similar to these used during their production cultivation, but without the traditional mineral fertilization, which was replaced with post-sewage waters from the local, industrial, mechanical-biological sewage plant with the following composition:

pH	8.77
Ca total	$< 1.79 \text{ g} \cdot \text{dm}^{-3}$
Mg total	$< 0.02 \text{ g} \cdot \text{dm}^{-3}$
K solved in water	$< 0.83 \text{ g} \cdot \text{dm}^{-3}$
Na total	$< 0.17 \text{ g} \cdot \text{dm}^{-3}$

The plots were irrigated 13–15 times during the vegetation period (May–October) with one dose of 15 dm^3 · m^{-2}.

After the vegetation period had finished in November, the plants were harvested and the amount of the yield was evaluated for both fresh plants and air-dried plants. The samples of soil and plants were dried and ground in the laboratory. After mineralization total contents of alkaline elements Ca, Mg, K and Na were determined in dry plant mass and in soil. Magnesium was determined with atomic absorption spectrophotometric method (F-AAS) on AAS-3 Carl Zeiss-Jena apparatus, and Ca, K, and Na were determined with atomic spectrophotometric method.

Results and discussion

Repetitive, seasonal irrigation with post-sewage waters that were rich in biogenes caused significant changes in the chemism of the analysed soil.

The changes were observed not only in the case of high contents of alkaline elements in the soil, but also corelations between them (Table 1). It is characteristic that potassium turned out to be the most basic element in both absolute quantities and relative quantities. Potassium constituted 40 % of the total contents of the analysed elements. The significant contents of magnesium in the soil were also characteristic – there was more magnesium than calcium. The mass of magnesium was over 1.40 $g \cdot kg^{-1}$, and constituted 35 % of the total contents of the alkaline elements. Considerably small amounts of calcium were observed – only 23 % of the total mass of this group of elements. There was also little sodium in the soil. The mass of sodium was below 0.1 $g \cdot kg^{-1}$, which was 2 % of the mass of all alkaline elements.

Table 1

Mean contents and structure of alkaline elements in soil

Plant	Alkaline elements								Sum	
	Ca		Mg		K		Na			
	$g \cdot kg^{-1}$	%	$g \cdot kg^{-1}$	%	$g \cdot kg^{-1}$	%	$g \cdot kg^{-1}$	%	$g \cdot kg^{-1}$	%
Miscanthus sacchariflorus	0.89	22	1.37	34	1.72	42	0.102	2	4.082	100
Calamagrostis epigejos	0.99	24	1.50	36	1.55	38	0.097	2	4.137	100
Mean value	0.94	23	1.44	35	1.63	40	0.099	2		

Table 2 reveals that potassium dominated in the biomass of the investigated grasses, and constituted on average 50 % of the whole mass of the analysed elements. However, it should be noted that there was a significant discrepancy in uptaking of potassium between *Miscanthus sacchariflorus* and *Calamagrostis epigejos*. *Calamagrostis epigejos* uptake over 5 $g \cdot kg^{-1}$ of potassium, which was 75 %, and *Miscanthus sacchariflorus* uptake only 24 % of the total mass of potassium. Similar discrepancies were observed in uptaking of calcium. *Miscanthus sacchariflorus* uptake over 60 %, whereas *Calamagrostis epigejos* exactly 1/10 of this mass. Despite high contents of magnesium in the soil, both grasses uptake small amounts of this element. On average, the plant biomass contained only over 10 % of the mass of magnesium. There was very little sodium observed in the plant material – its mass constituted only 1 % of the total mass of alkaline elements.

Table 2

Mean contents and structure of alkaline elements in plant biomass

Plant	Alkaline elements								Sum	
	Ca		Mg		K		Na			
	$g \cdot kg^{-1}$	%	$g \cdot kg^{-1}$	%	$g \cdot kg^{-1}$	%	$g \cdot kg^{-1}$	%	$g \cdot kg^{-1}$	%
Miscanthus sacchariflorus	5.66	62	1.16	13	2.22	24	0.041	1	9.081	100
Calamagrostis epigejos	0.49	7	1.21	17	5.43	75	0.046	1	7.176	100
Mean value	3.08	34	1.18	15	3.83	50	0.043	1		

The data presented in Table 3 reveals that the contents of calcium in the biomass were higher than in the soil. A clear discrepancy can be observed between uptaking of calcium by both grasses. *Miscanthus sacchariflorus* has 7 times higher mass of this element than in the soil. The calculations that were performer reveal that the plant material of *Miscanthus sacchariflorus* contained nearly 90 % of the total amount of calcium. A small amount of this element (10 %) was found in the soil in the form of a reserve. *Calamagrostis epigejos* showed a totally different demand for calcium. There was a smaller amount of this element found in the plant (33 % of the mass) than in the soil. Reduced uptaking of calcium from the soil by *Calamagrostis epigejos* left a considerable amount in the soil in the form of a reserve.

Table 3

Mean contents and proportional contents of calcium in soil and plant

Plant	Content of Ca					
	Soil		Plant		Sum	
	$g \cdot kg^{-1}$	%	$g \cdot kg^{-1}$	%	$g \cdot kg^{-1}$	%
Miscanthus sacchariflorus	0.89	14	5.56	86	6.45	100
Calamagrostis epigejos	0.99	67	0.49	33	1.48	100
Mean value	0.94	40	3.03	60		

Table 4 reveals that both *Miscanthus sacchariflorus* and *Calamagrostis epigejos* uptook magnesium, that abounded in the soil, in a similar, limited manner. Similar amounts of this element were found in the biomass of both grasses in absolute quantities as well as in relative quantities.

Table 4

Mean contents and proportional contents of magnesium in soil and plant

Plant	Content of Mg					
	Soil		Plant		Sum	
	$g \cdot kg^{-1}$	%	$g \cdot kg^{-1}$	%	$g \cdot kg^{-1}$	%
Miscanthus sacchariflorus	1.37	54	1.16	46	2.53	100
Calamagrostis epigejos	1.50	55	1.21	45	2.71	100
Mean value	1.44	55	1.19	45		

The results in Table 5 confirm the fact that potassium was uptaken from the soil by both grasses in highest, but varying, amounts. The greatest amounts of potassium were found in *Calamagrostis epigejos*. There was 78 % of potassium found in its biomass. Slightly smaller amounts of this element were uptaken by *Miscanthus sacchariflorus* (56 %). Nevertheless, this amount was significant – over 2 $g \cdot kg^{-1}$ of potassium.

Table 5

Mean contents and proportional contents of potassium in soil and plant

Plant	Content of K					
	Soil		Plant		Sum	
	$g \cdot kg^{-1}$	%	$g \cdot kg^{-1}$	%	$g \cdot kg^{-1}$	%
Miscanthus sacchariflorus	1.72	44	2.22	56	3.94	100
Calamagrostis epigejos	1.55	22	5.43	78	6.98	100
Mean value	1.63	33	3.83	67		

The results in Table 6 unanimously reveal that both grasses uptaken little amounts of sodium that was present in the soil. Considerable amounts of this element (60–70 %) remained in the soil in the form of a reserve. Both grasses uptaken similar amounts of sodium, 0.043 $g \cdot kg^{-1}$ on average, which constituted 31 % of the total contents of sodium.

Table 6

Mean contents and proportional contents of sodium in soil and plant

Plant	Content of Na					
	Soil		Plant		Sum	
	$g \cdot kg^{-1}$	%	$g \cdot kg^{-1}$	%	$g \cdot kg^{-1}$	%
Miscanthus sacchariflorus	0.102	71	0.041	29	0.143	100
Calamagrostis epigejos	0.097	68	0.046	32	0.143	100
Mean value	0.099	69	0.043	31		

Discussion

Chemical properties of podsolic soil that was used in the experiment were different from the properties of such soils found in natural environment. This was caused by the use of fertilization only with post-sewage waters from biological-mechanical sewage plant over consecutive vegetation periods. This sewage was specific because on of its main sources was miners' bath.

The conditions created in the experiment were good enough for the grasses to thrive properly, and the yield of the plant biomass did not differ from this found in literature, which was noted in the previous work of the authors [15].

The results of the analysis of the soil with regard to the contents of alkaline elements show proper supply of soils. A different amount of elements can be observed in the soil and plant, as well as their mutual corelation in both cases. It is also characteristic that both in the soil and the plant potassium dominated among the alkaline elements. The amounts of potassium were the highest of all the alkaline elements – 40 % of the mass of the alkaline elements in the soil, and 50 %, on average, in the biomass of both grasses. However, there was a significant discrepancy in the ability to store potassium by both grasses. In the case of *Calamagrostis epigejos* the contents of potassium were 75 % of the total contents of the analyzed element, and in *Miscanthus sacchariflorus* it was only 24 %. Low contents of potassium in *Miscanthus sacchariflorus* are confirmed by results obtained by other authors [15–17].

It was also characteristic for both grasses to uptake calcium and magnesium from the soil. In the soil the amount of magnesium (35 % of total amount of the alkaline elements) was greater than of calcium (slightly over 20 %), but in the biomass of both grasses these proportions were reversed. Calcium in plants constituted 34 % of the total mass of the alkaline elements, and magnesium 15 %. Considerable differences in uptaking of calcium were also observed. *Miscanthus sacchariflorus* retained as much as 86 % of this element (5.56 $g \cdot kg^{-1}$) and *Calamagrostis epigejos* only 33 % (0.49 $g \cdot kg^{-1}$). Similar amounts of calcium in *Miscanthus sacchariflorus* (5.56 $g \cdot kg^{-1}$) can be found in the experiments [1].

Uptake of sodium from the soil by the grasses was marginal. In the biomass only 31 % of the total contents of sodium were observed and the rest remained in the soil in the form of a reserve. Little amounts of sodium in energy plants are confirmed by the works of Kalembasa et al [17, 18].

The sum of alkaline element uptake in the biomass of *Miscanthus sacchariflorus* was 9 $g \cdot kg^{-1}$, and *Calamagrostis epigejos* absorbed 7 $g \cdot kg^{-1}$ of alkaline elements. Uptake abilities of the investigated grasses are not great when compared with other energy plants. Other works of the author [19] revealed that amounts of alkaline elements obtained with the same methods were: 18 $g \cdot kg^{-1}$ in the case of *Helianthus tuberosus*, and 12 $g \cdot kg^{-1}$ in the case of salix.

It should be noted, that there was a significant discrepancy in alkaline element uptake by both grasses. *Miscanthus sacchariflorus* has high capabilities to calcium uptake. This proves an observation that optimum soils for cultivation of this plant are V, and VI quality class soils, with reaction close to alkaline and contents of calcium in undersoil

[20]. The results that were obtained also prove an opinion that *Calamagrostis epigejos*, being a pioneer plant, often occurs on very acidic soils and does not require calcium for its growth, but mainly silica. The study reveals that under favorable growth conditions this plant uptake large quantities of potassium.

Conclusions

1. Both grasses show properties that are useful for combustion of biomass because they contain limited amounts of alkaline elements.
2. It was observed, that *Miscanthus sacchariflorus* and *Calamagrostis epigejos* have different qualitative and quantitative abilities to uptake alkaline elements from the soil with optimum contents of these elements. It was estimated, that *Miscanthus sacchariflorus* uptook 20 % more of the total mass of these elements than and *Calamagrostis epigejos*.
3. The basic element uptook by both grasses was potassium (on average 50 % in the composition of biomass) and calcium (34 %). The grasses uptook considerably less magnesium (15 %) and trace amounts of sodium (1 %).
4. There was a significant discrepancy in uptaking of alkaline elements by both grasses. *Miscanthus sacchariflorus* uptook 62 % of calcium and 24 % of potassium, and *Calamagrostis epigejos* retained 7 % of calcium and 75 % of potassium.

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CHEMICZNA OCENA SIANA WYBRANYCH TRAW W KONTEKŚCIE ICH PRZYDATNOŚCI W ENERGETYCE

Katedra Ochrony i Kształtowania Środowiska, Wydział Nauk Rolniczych w Zamościu,
Uniwersytet Przyrodniczy w Lublinie;
Instytut Przyrodniczo-Matematyczny, Państwowa Wyższa Szkoła Zawodowa w Zamościu

Abstrakt: Celem przeprowadzonych badań była ocena zawartości pierwiastków zasadowych w glebie i sianie traw w kontekście możliwości ich wykorzystania jako paliwa w piecach energetyki zawodowej. W badaniach wykorzystano 2 gatunki zdecydowanie różniących się traw: *Miscanthus sacchariflorus* oraz *Calamagrostis epigejos*. Doświadczenie założono na typowych dla północnej części Lubelszczyzny glebach bielicowych zaliczanych do IVb klasy bonitacyjnej w obiektach należących do Łęczyńskiej Energetyki w KWK Bogdanka. Rośliny uprawiane były w warunkach zbliżonych do produkcyjnych, ale bez tradycyjnego nawożenia mineralnego, które było zastąpione wodami pościelowymi z miejscowej oczyszczalni przemysłowej typu mechaniczno-biologicznego. Przeprowadzone badania wykazały, że obie trawy charakteryzują właściwości przydatne do spalania biomasy, bowiem zawierają ograniczone ilości pierwiastków zasadowych, przy czym wystąpiło wyraźne zróżnicowanie pobierania poszczególnych pierwiastków alkalicznych przez obie trawy.

Słowa kluczowe: trawa, siano, biomasa, miskant cukrowy, trzcinnik piaskowy, pierwiastki alkaliczne, woda pościekowa

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Małgorzata RAFAŁOWSKA[1]

ESTIMATION OF THE NITRATE(V) CONTENT IN THE SURFACE WATERS OF AN AREA PARTICULARLY EXPOSED TO POLLUTION FROM AGRICULTURAL SOURCES

OCENA ZAWARTOŚCI AZOTANÓW W WODACH POWIERZCHNIOWYCH OBSZARU SZCZEGÓLNIE ZAGROŻONEGO ZANIECZYSZCZENIAMI ZE ŹRÓDEŁ ROLNICZYCH

Abstract: The aim of the research was to estimate the concentrations and loads of nitrate nitrogen(V) as well as their seasonal changes in the waters flowing from the catchments qualified as areas in particular danger of nitrate pollution from agricultural sources. The tests were conducted in the years 2005–2007 in the catchment of Dobskie Lake. The research covered four parts of the Dobskie Lake catchment, in which the discharges and properties of the waters were established. Water samples for laboratory tests were collected once a month. Nitrate nitrogen(V) content and physicochemical parameters such as temperature, pH reaction, oxygen saturation and electrolytic conductivity were evaluated in the samples.

The obtained results indicate that intensified agricultural utilisation of the area causes a marked increase in the concentrations of nitrate nitrogen(V), in surface waters, particularly in drainage waters. The highest concentrations of N-NO_3 occur in winter (on average 17.38 mg $\cdot$ dm^{-3}) in drainage waters flowing from the intensively utilised area, and the lowest in watercourses, particularly in spring and summer (0.13–0.25 mg $\cdot$ dm^{-3}). The load of N-NO_3 flowing from the agricultural catchment depends on the meteorological conditions, the type of drainage system and the intensity of the catchment utilisation. A substantial part (about 45%) of the yearly charge of N-NO_3 occurs in wintertime. It is a result of an intensive inflow of nitrogen with the thawing snow and precipitation in the period of limited bioaccumulation.

The results of research indicate a potential negative influence of the waters flowing from agricultural areas, mostly through drainage systems, on the waters of Dobskie Lake. Considering high concentrations and loads of nitrates in the waters flowing into the lake, we can qualify it as exposed to eutrophication. This confirms the legitimacy of regarding the area as one where the flow of nitrogen from agricultural sources ought to be limited.

Keywords: surface waters, drains, nitrates, agricultural pollution

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[1] Department of Land Reclamation and Environmental Management, University of Warmia and Mazury in Olsztyn, pl. Łódzki 2, 10–957 Olsztyn, tel. 089 523 39 92, email: malgorzata.rafalowska@uwm.edu.pl

Numerous studies and tests indicate that in rural areas, agricultural activity is the main source of nitrates. Fertiliser components not fully utilised in farming, particularly nitrogen, can penetrate into ground and surface waters, causing their pollution. This pollution is of non-point type and can affect even 70% of the agriculturally utilised area of the country [1]. One of the first symptoms of pollution of the water environment by farming is the appearance of considerable, sometimes even large, amounts of nitrates in the groundwaters in rural areas [2–4]. The nitrogen excessively carried into waters causes an increase in their fertility, and as a result of eutrophication ie their unsuitability for consumption [5, 6].

The current regulations allow for nitrate concentrations not exceeding 50 mg $NO_3 \cdot dm^{-3}$ in the water suitable for consumption. In order to ensure proper quality of water supplies, actions have been taken to limit the inflow of nitrogen from agricultural sources [7]. These actions must be accompanied by monitoring the nitrate concentrations in waters as the first indicator of their effectiveness.

The aim of the research was to estimate the concentrations and loads of nitrates as well as their seasonal changes in the waters of the catchments qualified as areas particularly exposed to pollution from agricultural sources.

Material and methods of research

The research was conducted in the years 2005–2007 in the catchment of Dobskie Lake. Agricultural areas in the lake catchment are utilised by a farm which specialises in animal husbandry. The research covered four partial catchments of Dobskie Lake, which were different in terms of the intensity of utilisation, considering the fertilisation (intensive, moderately intensive and less intensive) and the type of a drainage system (ditches and drains – Fig. 1).

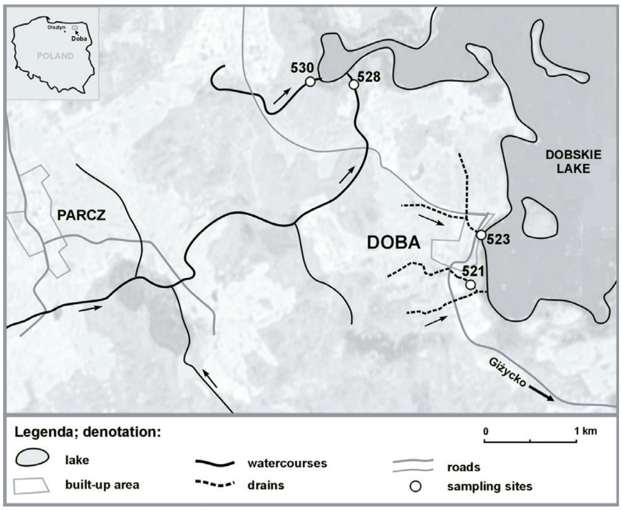

Fig. 1. Localisation of sampling sites in the catchment of Dobskie Lake

1) An intensively utilised area of a drainage catchment **(521)**, of 15.1 ha. In 2005, winter triticale was grown there. Mineral fertilisation (N – 61 kg · ha^{-1}) as well as organic fertilisation in the form of liquid manure in the amount of 20 m^3 · ha^{-1} · $year^{-1}$. In 2006, for the plantation of spring barley, the following fertilisation was used: 98 kg N · ha^{-1}, 46 kg P_2O_5 · ha^{-1}, 60 kg K_2O · ha^{-1}. In June 2006, it was observed that liquid manure was poured onto the land, which was not in accordance with good farming practice, and in fact against it. The catchment contains livestock buildings. In 2007, for the cultivation of winter rye 100 kg N · ha^{-1}, 52 kg P_2O_5 · ha^{-1}, 50 kg K_2O · ha^{-1} were used. Arable lands are located on moderately compact soils (strong loamy sands) classified as soil quality class IIIb and IVa.

2) A drainage zone **(523)** utilised with moderate intensity, located near the buildings of the village of Doba and an agricultural farm. A drainage pipeline removes water from fertilised arable lands. The fields were fertilised with – 68 kg N · ha^{-1}, 40 kg P_2O_5 · ha^{-1} and 55 kg K_2O · ha^{-1} in 2005 for the cultivation of oats, in 2006 for the cultivation of rye: 88 kg N · ha^{-1}, 41 kg P_2O_5 · ha^{-1} and 54 kg K_2O · ha^{-1}. In 2007, winter rye was sown in the fields and the following fertilisation was used: 140 kg N · ha^{-1}, 52 kg P_2O_5 · ha^{-1} and 50 kg K_2O · ha^{-1}. Near this drainage zone, recreational plots and a village settlement are situated. The soils are light and classified as the quality class V. The catchment area is 41.7 ha.

3) An intensively utilised catchment of a watercourse (528) covers the areas supplied by the bay of Pilwa, situated in the western part of Dobskie Lake. The surface watercourse removes water from a substantial area of 1616 ha, covered with forests in 57 %. In the period from July to October 2005, a disappearance of flow in this watercourse was noted, as well as in July and August 2006. Arable lands located in this catchment are mainly light loamy sands (soil class IV b). On these lands, triticale was cultivated in 2005, in 2006 – winter rape, and in 2007 – winter wheat. In the test period, the following fertilization was used: in 2005 – 130 kg N · ha^{-1} and in spring liquid manure 20 m^3 · ha^{-1}, in 2006 – 206 kg N · ha^{-1}. In 2007, for the cultivation of winter wheat, the following amounts of fertilisers were used: 130 kg N · ha^{-1}, 52 kg P_2O_5 · ha^{-1}, 54 kg K_2O · ha^{-1}.

4) The catchment of a watercourse (530) utilised with moderate intensity, removing water from the land of western part of the bay of Pilwa. The area of this territory is 109 ha and it is covered by forests in 60 %. The remaining part contains arable lands on light clay sands. In the analysed test period, a tendency of periodic disappearance of the water flow in the watercourse was noted in the summer and autumn. In 2005, only mineral fertilisation for the cultivation of oats was used in the amounts of 100 kg N · ha^{-1} and 60 kg P_2O_5 · ha^{-1}, 50 kg K_2O · ha^{-1}, and in 2006 and 2007 rye was cultivated using respectively 113 kg N · ha^{-1}, 44 K_2O · ha^{-1} and 136 kg N · ha^{-1}, 52 kg P_2O_5 · ha^{-1}, 50 kg K · ha^{-1}.

According to the guidelines for the implementation of the Nitrates Directive [8], these catchments are a part of a particularly endangered area, where the discharge of nitrogen from agricultural sources should be limited. The area was delineated on the basis of nitrate concentration in underground waters reaching 95 mg · dm^{-3} [9].

Within the conducted on-site tests, physicochemical parameters of the water were measured: the pH reaction with a potentiometer, temperature with a thermometer integrated with an oxygen probe, oxygen saturation with a WTW Multiline P3 meter, electrolytic conductivity with a Hanna conductometer. The measurements of the discharge of drainage waters and watercourses supplying the lake were made during sampling with an electromagnetic VALEPORT flow-meter model 801. The water samples for laboratory analyses were collected once a month in the years 2005–2007 and the content of nitrate nitrogen(V) was determined in them using colorimetry with phenoldisulphonic acid. The test was conducted in accordance with the generally accepted method [10].

The seasonal variability of water flow and concentrations as well as the load of nitrate nitrogen(V) was calculated on the basis of a division of the collected samples according to the time of sampling: winter (January–March), spring (April–June), summer (July–September), autumn (October–December). The amount of the nitrate flow was calculated by multiplying the concentration by the volume of the water flow. Then, in order to calculate the amount of outflow from 1 ha, the previously calculated amount was divided by the area of the drained ground.

Results and discussion

Nitrate nitrogen(V) in the natural environment come mainly from the atmosphere and get into the surface waters with the rainfall and with the runoff of surface and groundwaters from the catchment. It was counted that, depending on the amount of precipitation, 1 ha of ground area is supplied with 2 to 6 kg of nitrogen a year, which is only a small fraction compared with fertilization and microbiological bonding of atmospheric nitrogen [11]. A part of the nitrogen from the soil flows into the water as well. Mineral nitrogen compounds are easily soluble, so they flow from the catchment mainly in the form of a solution [12]. The concentration of $N\text{-}NO_3$ in groundwaters in agricultural areas, coming from local sources, mainly from the soil, is reflected in the waters of drainage systems [13]. The amount and dynamics of water flow and the content of compounds depend largely on meteorological conditions (Fig. 2).

Considering the amount of precipitation[14], a normal year (2005 – 545 mm) and two wet years (2006 – 640 mm; 2007 – 646 mm) were distinguished.

Also a high variability of air temperature was noted – its average value in the subsequent years was 7.7, 8.1 and 8.8 ^{o}C, respectively.

During the whole test period, a tendency for the periodic drying out of some flows was observed in the summer and at the beginning of autumn. The subzero air temperatures, persisting from December 2005 to March 2006 and in February 2007, preserved the precipitation water on the ground surface in the form of snow and ice. It was activated in April 2006 and in March 2007, which was conducive for the nitrates being washed out of the ground into the drainage systems. As a consequence, in the waters from the drain removing water from the intensively utilised area, in the year 2005 (a normal one) in winter the average seasonal concentration of $N\text{-}NO_3$ was 30 % higher than in 2006 (a wet year) and 65 % higher in the summer. In sum, it should be

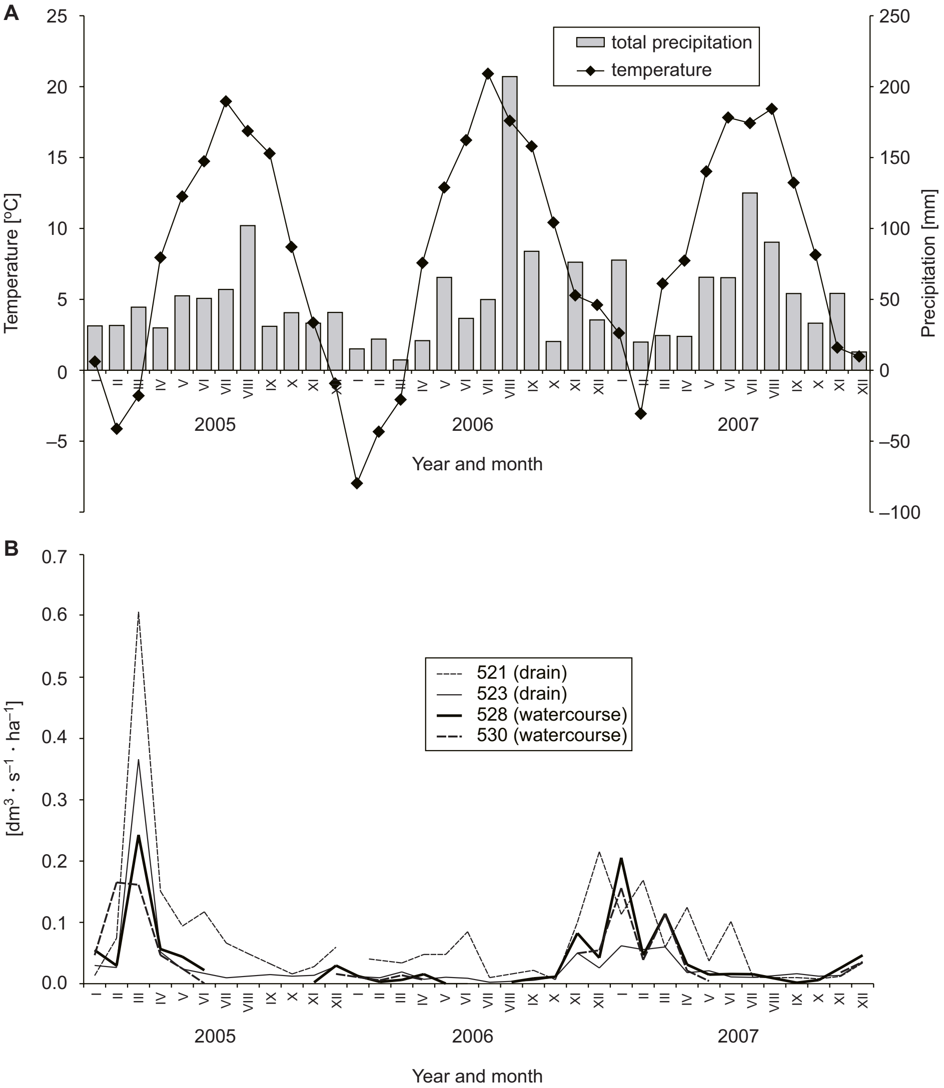

Fig. 2. Distribution of precipitation and air temperature (A) and the water runoff from the tested catchments (B) in the years 2005–2007

stated that water removal by means of drains increases the outflow of water within the year also in the summer. When water is removed by watercourses, the outflow is only slight, and sometimes it disappears.

The water from both the drains and the ditches was sufficiently saturated with oxygen throughout the whole test period, except for the water from a watercourse removing water from the area utilised with moderate intensity (no flow in the summer) which influenced the process of nitrification (Table 1).

Table 1

Seasonal variability of physicochemical parameters in the tributaries of Dobskie Lake in the years 2005–2007

Parameters / Inflow (way of land utilisation)	Season	Oxygen saturation [%]	Temperature [°C]	pH	Conductivity [μS/cm]
521 drain (intensive)	W*	58.3	4.5	7.2	762
	S	50.2	11.3	7.2	762
	Su	62.0	14.2	7.3	798
	A	62.0	7.5	7.3	815
	Y	58.1	9.1	7.3	782
523 drain (moderately intensive)	W	91.3	4.5	7.5	638
	S	84.4	9.6	7.6	672
	Su	92.4	13.6	7.6	681
	A	93.3	8.5	7.5	690
	Y	89.6	8.8	7.6	669
528 watercourse (intensive)	W	75.6	1.0	7.3	611
	S	73.0	17.0	7.8	612
	Su	86.0	15.4	7.7	550
	A	63.7	3.8	7.4	578
	Y	73.6	8.2	7.5	595
530 watercourse (moderately intensive)	W	89.2	1.3	7.7	580
	S	93.7	14.4	7.9	597
	Su	No flow			
	A	84.0	3.2	7.7	663
	Y	88.3	6.3	7.8	609

* W – winter; S – spring; Su – summer; A – autumn; Y – year

The saturation of water with oxygen corresponded with high variability of electrolytic conductivity of the water (550 – 815 μS · cm^{-1}). Its variable values can be a sign of a high content of substances dissolved in water, particularly in autumn. Besides, the increased values of electrolytic conductivity of the waters flowing through drainage systems, particularly form the intensively utilised area, indicate that large amounts of mineral substances from local sources penetrate into them as a result of using mineral and organic fertilizer as well as of the decomposition of organic matter in the soil. The pH values during the test period were changing just slightly, as opposed to the electrolytic conductivity. The water reaction value in the intensively utilised areas is lower than in other test sites (on average pH = 7.3) which shows that soils are more prone to acidification, and the processes occurring in the soil are aimed at mineralisation, which was reflected in the increased electrolytic conductivity.

The variability of N-NO_3 concentrations in the waters flowing out of agricultural catchments is a result of numerous factors. The most important ones include the intensity of utilisation, the type of a drainage system and meteorological conditions. The above-mentioned factors in the analysed test period caused a high variability of N-NO_3

Table 2

Characteristics of N-NO_3 concentrations [mg · dm^{-3}] in the waters supplying Dobskie Lake in the years 2005–2007

Type of inflow Way of land utilisation	2005			2006			2007			Average from the test years		
	X average range of values	SD standard deviation	Coefficient of variability [%] CV	X average range of values	SD standard deviation	Coefficient of variability [%] CV	X average range of values	SD standard deviation	Coefficient of variability [%] CV	X average range of values	SD standard deviation	Coefficient of variability [%] CV
Drain (521) intensive	17.66 7.10–32.40	7.77	44.00	11.56 4.24–18.30	4.50	38.94	14.39 2.04–21.20	5.64	39.20	14.53 2.04–32.40	6.47	44.26
Drain (523) Moderately intensive	11.27 1.21–17.90	5.48	48.62	14.67 11.10–17.30	2.24	15.26	9.57 0.58–13.60	4.55	47.58	11.84 0.58–17.90	4.70	39.69
Watercourse (528) intensive	0.83 0.10–3.70	1.17	141.08	0.366 0.10–0.80	0.26	72.17	0.986 0.10–5.72	1.70	172.67	0.73 0.10–5.72	1.22	166.57
Watercourse (530) Moderately intensive	2.02 0.28–6.32	2.01	99.36	1.062 0.47–1.43	0.36	33.51	2.10 0.05–5.56	1.96	93.13	1.73 0.05–6.32	1.69	93.98

concentrations considering both the differences between particular years and the yearly distribution of values (Tables 2, 3).

Table 3

Average seasonal concentrations of N-NO_3 [mg · dm^{-3}] in the inflows of Dobskie Lake in the years 2005–2007

Season	Type of inflow (way of land utilisation)	Year			Average from the test years
		2005	2006	2007	
Winter	521 drain (intensive)	19.23	13.90	19.00	17.38
	523 drain (moderately intensive)	10.90	14.60	8.39	11.30
	528 watercourse (intensive)	1.44	0.48	3.08	1.67
	530 watercourse (moderately intensive)	3.41	1.14	3.89	2.81
Average		**8.75**	**7.53**	**8.59**	**8.29**
Spring	521 drain (intensive)	12.17	7.41	11.90	10.49
	523 drain (moderately intensive)	9.34	15.83	5.79	10.32
	528 watercourse (intensive)	0.43	0.17	0.16	0.25
	530 watercourse (moderately intensive)	0.89	0.47	0.61	0.66
Average		**5.70**	**5.97**	**4.62**	**5.43**
Summer	521 drain (intensive)	24.10	8.88	16.90	16.63
	523 drain (moderately intensive)	9.25	15.50	12.15	12.30
	528 watercourse (intensive)	no water	0.13	0.13	0.13
	530 watercourse (moderately intensive)	no water	no water	no water	no water
Average		**16.68**	**8.17**	**9.73**	**9.68**
Autumn	521 drain (intensive)	17.27	15.93	10.58	14.59
	523 drain (moderately intensive)	14.93	13.03	12.80	13.59
	528 watercourse (intensive)	0.53	0.53	0.29	0.45
	530 watercourse (moderately intensive)	1.27	1.29	0.92	1.16
Average		**8.50**	**7.70**	**6.15**	**7.45**
Year	521 drain (intensive)	17.65	11.56	14.39	14.53
	523 drain (moderately intensive)	11.27	14.67	9.57	11.84
	528 watercourse (intensive)	0.83	0.37	0.99	0.73
	530 watercourse (moderately intensive)	2.03	1.06	2.10	1.73
Average		**7.95**	**6.92**	**6.76**	**7.21**

Considering the easy washing-out from the ground and the active participation in biogeochemical processes, the level of nitrates in waters is subject to substantial fluctuations during the test period [15]. Analysing the dynamics of N-NO_3 concentrations (in relation to the above-mentioned factors) in the drainage outlets, the greatest fluctuations from 7.10 to 32.40 mg · dm^{-3} (SD = 7.77, CV = 44.00 %) in 2005 and from 2.04 to 21.20 mg · dm^{-3} (SD = 5.64, CV = 39.20 %) in 2007 were noted in the waters from the drainage removing water from the intensively utilised area (Table 2). In the waters of the intensively utilised watercourse, the highest variability coefficient was noted – CV = 172.62 % with the concentrations from 0.10 to 5.72 mg · dm^{-3} in 2007.

Such high average seasonal concentration values from the three years were influenced by the situation in 2005, when liquid manure was used in the intensively utilised catchment area from which water was removed through a drainage network.

It was also noted that the agricultural utilisation of arable lands where water was removed by drains, in comparison with the watercourse removal, causes a more than sevenfold increase in $N\text{-}NO_3$ concentration in drainage outflows. During the whole test period, a noticeable seasonal variability occurred. The highest concentration of $N\text{-}NO_3$ was noted in winter and summer, respectively 17.38 and 16.63 $mg \cdot dm^{-3}$ on average in the waters of a drain removing water from the intensively utilised area (Table 3). Such high nitrate(V) concentrations during the three-year research period can be explained by the easy washing out of this compound from the ground and by its active participation in biochemical processes. During the whole test period, the lowest concentration of nitrates was observed in the summer – on average 0.13 $mg \cdot dm^{-3}$ in the water flowing into Dobskie Lake through a watercourse (528) characterised by the occurrence of marshy areas in the catchment, which separate it from agriculturally utilised fields.

The nitrate content in the waters of drainage systems is a result of not only hydrological and meteorological conditions, but also of plant growth intensity [16]. Therefore, a lower concentration of nitrates in the waters of the agricultural catchment was observed on the time of intensive plant growth, as a consequence of the running out of supplies of easily accessible forms of biogenic compounds in the soil and water.

A high concentration of nitrates(V) in the tested water, mostly from drainage sources, contributed to the lowering of the water quality class. The average concentration of $N\text{-}NO_3$ allows to qualify the tested water from the area from which water was removed by the drainage network and which was utilised intensively and with moderate intensity, to quality class V (bad), and the area drained with surface watercourses was qualified as water quality class II (good) [17].

Depending on the meteorological (seasonal) conditions, the intensity of farming (fertilization) and the drainage system in the area, the outflow of $N\text{-}NO_3$ ranged from below 0.02 $kg \cdot ha^{-1}$ in the summer (the watercourse) to 11.81 $kg \cdot ha^{-1}$ in winter (the drain – Table 4). Two processes contributed to it – a decreased outflow of waters, or even the disappearance of it in the summer, and a better utilisation of nitrogen by plants during the vegetation season. The bulk of the carried load (about 45 %) of $N\text{-}NO_3$ occurs in wintertime. It is a result of the catchment being supplied with freeze-thaw water, characterised by an increased content of this form of nitrogen. It is also due to the lack of vegetation, and therefore of phytosorption, including the sorption of nitrogen compounds.

However, considering the annual discharge of $N\text{-}NO_3$, its greatest load of 26.65 $kg \cdot ha^{-1}$ was noted in the waters from the drainage outlet in an intensively utilised area, and the lowest of 2.32 $kg \cdot ha^{-1}$ in the waters of a watercourse draining an intensively utilised area. In comparison with the watercourses, the annual load of $N\text{-}NO_3$ in the waters of the drainage network was on average 10 times higher. It was probably caused by the more intensive water removal and oxygen saturation of the soils, as well as the lower biological sorption of nitrogen in the drainage system [13]. The yearly distribution of meteorological conditions causing the variability of water runoff is also important. Therefore, in 2005 (on average 14.43 kg · ha^{-1}) the outflow was 30 % higher than in 2007 (on average 10.61 kg · ha^{-1}) and 3 times higher than in 2006.

Table 4

Seasonal and annual variability [kg · ha^{-1} · $year^{-1}$]
of the specific runoff of $N\text{-}NO_3$ from the test area

Season	Type of inflow (way of land utilisation)	Year			Average from test years
		2005	2006	2007	
Winter	521 drain (intensive)	16.33	2.53	16.59	11.81
	523 drain (moderately intensive)	6.60	1.60	3.82	4.00
	528 watercourse (intensive)	2.49	0.02	3.96	2.16
	530 watercourse (moderately intensive)	3.70	0.06	3.41	2.39
Average		**7.28**	**1.05**	**6.94**	**5.09**
Spring	521 drain (intensive)	11.35	3.19	8.10	7.55
	523 drain (moderately intensive)	2.64	1.10	0.89	1.55
	528 watercourse (intensive)	0.14	0.01	0.02	0.06
	530 watercourse (moderately intensive)	0.26	0.01	0.05	0.10
Average		**3.60**	**1.08**	**2.26**	**2.31**
Summer	521 drain (intensive)	7.08	0.78	0.90	2.92
	523 drain (moderately intensive)	0.66	0.33	0.84	0.61
	528 watercourse (intensive)	no water	< 0.01	< 0.03	< 0.02
	530 watercourse (moderately intensive)	no water	no water	no water	no water
Average		**3.87**	**0.37**	**0.58**	**1.18**
Autumn	521 drain (intensive)	4.41	5.53	1.50	3.81
	523 drain (moderately intensive)	2.00	2.21	2.10	2.10
	528 watercourse (intensive)	0.03	0.18	0.08	0.09
	530 watercourse (moderately intensive)	0.05	0.15	0.17	0.12
Average		**1.62**	**2.01**	**0.96**	**1.53**
Year	521 drain (intensive)	39.16	13.70	27.09	26.65
	523 drain (moderately intensive)	11.90	5.87	7.65	8.47
	528 watercourse (intensive)	2.65	0.24	4.07	2.32
	530 watercourse (moderately intensive)	4.01	0.26	3.63	2.63
Average		**14.43**	**5.02**	**10.61**	**10.02**

Conclusions

1. The concentrations and loads of nitrates flowing from agricultural catchments depend on meteorological conditions and the drainage system, which affect the scale and dynamics of water flow, as well as on the intensity of land utilisation.
2. The draining increases the flow of water twice and of nitrates 4–13 times compared to the water removal with open watercourses.
3. The intensification of agricultural utilisation of the area causes a marked increase of nitrate nitrogen(V) concentrations in surface waters, particularly in drainage waters.

The highest concentrations of N-NO_3 occur in winter (on average 17.38 mg · dm^{-3}) in drainage waters flowing from an intensively utilised area, and the lowest in watercourses, particularly in spring and summer (0.13-0.25 mg · dm^{-3}).

4. A substantial part (about 45 %) of the annual load of N-NO_3 occurs in wintertime. It is a result of an intensive flow of nitrogen with freeze-thaw water and precipitation water in the period of limited bioaccumulation. During winter frosts and summer droughts the outflow is minimal because of a periodic disappearance of water flows.

5. The research results indicate a potential negative influence of waters flowing out of agricultural areas, mostly through drainage systems, on the waters of Dobskie Lake. Considering the high nitrate concentrations in the waters flowing into the lake, it can be said it is endangered with eutrophication. This confirms that this area should be regarded as one where the outflow of nitrogen from agricultural sources ought to be limited.

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OCENA ZAWARTOŚCI AZOTANÓW W WODACH POWIERZCHNIOWYCH OBSZARU SZCZEGÓLNIE ZAGROŻONEGO ZANIECZYSZCZENIAMI ZE ŹRÓDEŁ ROLNICZYCH

Katedra Melioracji i Kształtowania Środowiska,
Uniwersytet Warmińsko-Mazurski w Olsztynie

Abstrakt: Celem badań była ocena stężeń i ładunków azotu azotanowego(V) oraz określenie sezonowych ich zmian w wodach odpływających ze zlewni zakwalifikowanych do obszarów szczególnie narażonych na zanieczyszczenia wód azotanami ze źródeł rolniczych. Badania prowadzono w latach 2005–2007 w zlewni Jeziora Dobskiego. Badaniami objęto cztery zlewnie cząstkowe jeziora Dobskiego, w których określono przepływy i właściwości wód. Próbki wód do analiz laboratoryjnych pobierano raz w miesiącu i oznaczano w nich azot azotanowy(V) oraz parametry fizykochemiczne: temperaturę, odczyn, nasycenie tlenem, przewodność elektrolityczną.

Uzyskane wyniki świadczą o tym, że intensyfikacja rolniczego użytkowania terenu powoduje wyraźny wzrost stężeń azotu azotanowego(V) w wodach powierzchniowych szczególnie w wodach drenarskich. Największe stężenia N-NO_3 występują zimą (średnio 17,38 mg · dm^{-3}) w wodach drenarskich odpływających z obszaru intensywnie użytkowanego a najmniejsze w ciekach szczególnie wiosną i latem (0,13–0,25 mg · dm^{-3}). O ładunku N-NO_3 odpływającego ze zlewni rolniczej decydują warunki meteorologiczne, rodzaj systemu melioracyjnego oraz intensywność użytkowania zlewni. Zasadnicza część (około 45 %) rocznego ładunku N-NO_3 przypada na okres zimowy. Jest to skutkiem intensywnego odpływu azotu wraz z wodami roztopowymi i opadowymi w okresie ograniczonej bioakumulacji.

Wyniki badań wskazują na potencjalny negatywny wpływ wód odpływających z terenów rolniczych, szczególnie systemami drenarskimi na wody jeziora Dobskiego. Ze względu na duże stężenia i ładunki azotanów w wodach dopływających do jeziora można ocenić je jako narażone na eutrofizację. Potwierdza to zasadność uznania tego terenu za obszar, z którego odpływ azotu ze źródeł rolniczych należy ograniczyć.

Słowa kluczowe: wody powierzchniowe, dreny, azotany, zanieczyszczenia rolnicze

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Piotr SKOWRON and Monika SKOWROŃSKA[1]

DISSOLVED ORGANIC CARBON CONCENTRATIONS IN DRAINAGE WATERS AND SOILS FROM AGRICULTURAL ECOSYSTEMS

ZAWARTOŚĆ ROZPUSZCZALNEGO WĘGLA ORGANICZNEGO W WODACH DRENARSKICH I GLEBACH Z EKOSYSTEMÓW ROLNICZYCH

Abstract: The two-year field and laboratory experiments were carried out to investigate the influence of soil management, land use, climate conditions and soil properties on dissolved organic carbon (DOC) concentrations in drainage waters and soils. In the field experiment drainage waters were sampled from 12 drainage watersheds (in four research areas characterized by different soil properties each with three research sites – drainage watersheds were chosen each located in area differing in terms of land use and management practices). In the laboratory study pH values (3.5–7.5) typical for Polish soils were simulated in the soils sampled from the four research areas and DOC concentration was determined. It was found that DOC concentration may increase as the result of FYM an NPK fertilizer application, temperature rise and rainfall (during summer), as well as being depended on the soil properties (percentage of particles with a diameter below 0.02 mm, content of phosphorus and pH value). However the influence of individual factors on DOC concentration might be difficult to predict under field conditions due to their overlapping.

Keywords: DOC, drainage waters, soil management, soil properties

Dissolved organic matter (typically measured as dissolved organic carbon and hereafter referred to as DOC) is a ubiquitous component, present in all ecosystems, operationally defined as comprising any organic compound passing through a 0.45 μm filter. Some DOC molecules can be identified chemically (such as organic acids, sugars, amino acids, fats, carbohydrates, and proteins), however most of them have no readily identifiable structure, and are known under the collective term “humic substances” [1–3]. The chemical composition of DOC fractions indicates that DOC consists mainly of by-products of organic matter mineralization and of products of microbial synthesis [2, 4]. Although dissolved organic carbon accounts for only a small proportion of the total organic carbon, which it tends to be in equilibrium with, it is recognized as

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[1] Department of Agricultural and Environmental Chemistry, University of Life Sciences in Lublin, ul. Akademicka 15, 20–950 Lublin, tel. 81 445 69 95, fax 81 445 66 64, email: monika.skowronska@up.lublin.pl

a component that influences soil biological activity, affects the transport of metals and organic pollutants as well as cycling of nutrients and contributes to mineral weathering and podzolization [2, 4–7]. With these complex functions the ecological significance of DOC is not only restricted to the soil. It is also environmentally relevant for hydrosphere. Dissolved organic carbon affects the functioning of aquatic ecosystems through its influence on acidity, trace metal transport, light absorbance and photochemical properties, and energy or nutrient supply [1, 3]. In waters, DOC is assumed to be of predominately allochthonous origin, ie derived externally from terrestrial organic matter, and forms a significant component of the global carbon cycle. Numerous studies have shown increasing levels of DOC in the leachates from agricultural catchments. Flow paths of soil water with DOC are mainly determined by the distribution of the soils in relation to the drainage system. The linkage of DOC originated from the soil with the drainage system is temporally dynamic, depended on (i) intrinsic DOC quality parameters (molecular size, chemical structure, spectroscopic properties, and polarity), (ii) soil solution properties (nutrients, salts, ionic strength, pH, metals, organic compounds and microbial degrader community) and (iii) external factors (environmental factors – climate, landscape, hydrology; soil management – tillage, fertilization, liming, field crops; and land use – forest, grassland, arable) [2, 6–8].

In the present study, field and laboratory experiments were carried out to investigate the influence of management practices, land use, climate conditions and soil properties on dissolved organic carbon concentrations in drainage waters and soils.

Material and methods

The two-year field experiment was carried in four research areas: Osiny (gmina Żyrzyn*), Ownia (gmina Ryki*), Majdan Krasieniński (gmina Niemce*), and Zalesie (gmina Nowodwór*), situated on the cultivated soils typical for the Lubelskie region and characterized by different soil properties (Table 1). In these areas three research sites as an experimental unit (drainage watersheds with the final drainage wells ∅ 1 m) were chosen each located in the area differing in terms of land use and management practices (Table 2). Soil samples were collected from 0–30 cm, 30–60 cm and 60–90 cm layers at the beginning of the experiment and analyzed for the following properties: soil pH determined in H_2O and 1 M KCl according to the potentiometric method, the hydrolytic acidity (Hh) by the Kappen method, full water capacity by the weight method, soil texture according to the Bouyoucos method modified by Casagrande and Prószyński, contents of exchangeable cations by the F-AAS method (atomic absorption spectrometry with flame atomization) after 1 M CH_3COONH_4 extraction, the content of available P by the colorimetric method, and available K by the F-AAS method, after extraction according of the Egner-Riehm method (DL), the content of available Mg – by the F-AAS method after 0.0125 M $CaCl_2$ extraction.

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* Local Administrative Units – LAU 2

Table 1

The soil properties in the research areas

Site	Soil type	Maximum water capacity [%]	pH_{KCl}	Percentage [%] of fraction with ∅ < 0.02 mm	Available forms $[mg\ kg^{-1}]$		
					P	Mg	K
Osiny	Light loam	35.37	5.53	17.83	233.26	95.75	138.23
Ownia	Sandy loam	27.94	3.98	18.50	94.26	76.75	94.64
Majdan	Silit loam	43.21	4.27	41.66	19.86	66.75	58.32
Zalesie	Sandy loam	35.20	5.38	17.33	37.31	54.00	31.34

Table 2

The research site specification

Site	Watershed area [ha]	Livestock $[LU^{*} \cdot ha^{-1}\ yr^{-1}]$	FYM 1998–2000 $[Mg \cdot ha^{-1}\ yr^{-1}]$	NPK fertilization 1998–2000 $[kg \cdot ha^{-1}\ yr^{-1}]$
Osiny 1	7.2	0	0	240
Osiny 2	11.4	0	0	170
Osiny 3	6.4	0	0	75
Ownia 1	5.0	8.0	48	310
Ownia 2	18.36	2.8	25	220
Ownia 3	28.16	0.5	6	80
Majdan 1	0.4	5.4	53	260
Majdan 2	4.48	1.4	10	175
Majdan 3	15.12	0.8	10	75
Zalesie 1	13.3	1.1	10	240
Zalesie 2	2.76	0.7	6	135
Zalesie 3	17.19	2.2	12	110

* LU – Livestock Unit

Drainage water samples (1 dm^3 volume) were taken from each drainage watershed four times a year (in the early spring – beginning of the vegetation period, in the early summer – maximum biological activity of agricultural ecosystems, in the late autumn – the end of the vegetation period, and after harvest). All the samples were refrigerated until analysis of DOC concentrations were made (after the removal of inorganic carbon – by acidifying the sample, the DOC concentrations were determined by the conversion of organic carbon to CO_2 by an ultraviolet (UV) digester with detection of CO_2 using an infrared (IR) analyzer).

The net monthly precipitation (Fig. 1) was calculated as the difference between the monthly precipitation and the field reference evapotranspiration – FRE, on the basis of the data obtained from the Institute of Meteorology and Water Management (IMGW),

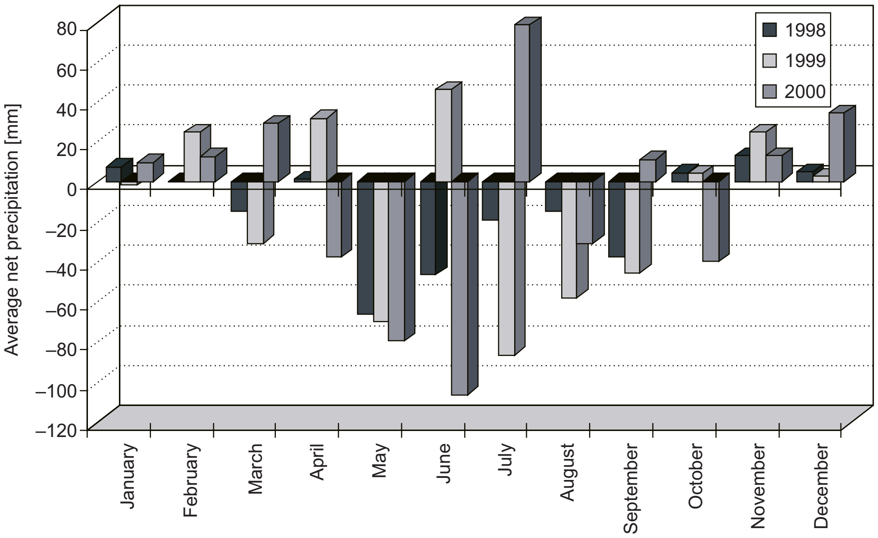

Fig. 1. Average net precipitation in the research areas

the Institute of Soil Science and Plant Cultivation (IUNG) and employing a mathematical model based on the Penman-Monteith equation for the FRE calculation. Areas and system of drainage watersheds were traced with the use of drainage maps from Lubelskie province Boards for Amelioration and Hydraulic Structures (WZMiUW). Data used for the analysis of soil management (rates of fertilizer applied, number of livestock, crop rotation) was gathered during surveys, by interviewing the farmers in the studied area. On the basis of the results characterized the livestock farmed and literature manure application rates were estimated (Table 2).

In the laboratory study pH values (3.5–7.5) typical for Polish soils were simulated in the soils sampled from the four research areas (0–20 cm). The soil materials were sieved (1 mm) and placed in plastic cups (250 g of soil was an experimental unit). The pH values of the soil samples were adjusted to a range 3.5–7.5 using 1 M and 0.1 M HCl as well as 1 M NaOH; 60 % of full water capacity was being maintained during six month-period of the incubation. At the end of the incubation soil samples were collected and analyzed for DOC concentration using an infrared (IR) analyzer.

The data were subjected to the double classification analysis of variance with two factors (site and sampling time in the case of DOC concentrations in drainage waters and area and pH in the case of DOC concentrations in soils), followed by Tukey's honest significance test; for the estimation of missing data Yeat's method was applied. The simple correlation method was used for the estimation of the relationships between DOC, P and N concentrations in drainage waters (field experiment), as well as DOC and H^+ concentrations in soils. In both, the field as well as the laboratory experiments pH values were logarithmically transformed into H^+ concentrations for the statistical purposes.

Results and discussion

Dissolved organic carbon concentrations in drainage waters are shown in Table 3 and reflects the balance between a wide variety of competing processes that produce and consume DOC.

Table 3

DOC concentrations [mg dm^{-3}] in drainage waters

Site	Sampling time							$\overline{X}$
	autumn 1998	spring 1999	summer 1999	autumn 1999	spring 2000	summer 2000	after harvest 2000	
Osiny 1	4.95	5.52	5.76	4.87	6.66	—*	8.60	6.20 abc**
Osiny 2	8.24	7.67	7.03	6.39	8.70	—	10.70	8.27 bc
Osiny 3	7.08	8.13	10.04	—	8.25	—	9.24	8.63 bc
Ownia 1	5.06	8.21	28.78	22.97	8.98	—	—	14.95 d
Ownia 2	14.67	4.11	5.49	—	4.76	—	—	7.33 abc
Ownia 3	4.54	4.92	9.99	—	4.12	—	—	5.96 abc
Majdan 1	7.66	4.68	4.09	6.84	3.37	4.05	4.72	5.06 a
Majdan 2	4.03	6.19	7.78	—	—	—	—	5.70 abc
Majdan 3	—	3.17	8.76	—	2.76	6.46	—	4.96 ab
Zalesie 1	5.40	6.94	4.80	3.65	4.30	4.50	2.59	4.60 a
Zalesie 2	6.75	8.84	12.20	5.28	12.44	—	—	9.25 c
Zalesie 3	7.58	15.80	9.20	3.23	5.89	11.27	4.46	8.20 bc
$\overline{X}$	6.68 a	7.02 a	9.49 b	6.95 a	6.23 a	8.29 ab	7.32 ab	7.43

* Mark (—) indicates lack of water in the drainage well;
** Different letters following the figures indicate belonging to homogenic groups in variance analysis.

Dissolved organic C export from the drained sites increased significantly under conditions of the over-application of FYM (farmyard manure) along with mineral fertilizers (Ownia 1). The high value of DOC observed in this watershed can also be related to the short duration between FYM application and sampling time. Much of the organic carbon added with organic amendments is degraded and transformed by microbial activity within 4–5 weeks [9]. The immediate impact of the organic material application on the increase in DOC level in soil could take place either directly, due to the addition of soluble organic compounds already present in the applied manure (organic carbon in the water extract of FYM represents about 6 % of the total organic carbon content), or indirectly by changing soil properties such as pH, nitrogen and phosphorus content and microbial activity, which might induce the dissolution of indigenous soil organic matter [4, 6, 9–12]. It ought to be stressed that since the DOC losses in drainage waters increased in the soils amended with high doses of FYM and DOC is a primary source of N and P (significant correlations between DOC and concentrations of $P\text{-}PO_4$ – $r = 0.84$ and $N\text{-}NH_4^+$ – $r = 0.84$ – Fig. 2, A-B), they may be the cause of accelerating the water eutrophication in the Ownia 1 watershed.

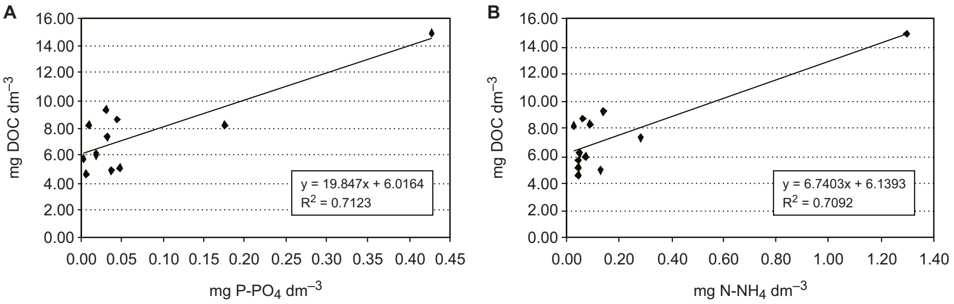

Fig. 2. Relationship between DOC and concentrations of P-PO$_4$ (A) and N-NH$_4$ (B) in drainage waters

In the case of Osiny sites 1–3 (treated only with mineral fertilizers, without manuring), DOC concentrations in leachates were generally above average value, suggesting that other factors, such as mineral fertilization or field crops may have been important in controlling DOC transfer. Increased crop dry matter productivity, which is proportional to N application, leads to greater returns of organic matter to the soil via plant residues and rhizodeposition. The high doses of phosphorus fertilizers (Osiny 1), applied before the experiment began, may have been responsible for a decline in DOC concentration due to the reduction in DOC sorption and in consequence its intensive leaching. It should be underlined that under agroecosystems with superiority of arable cropping (Osiny 2, 3), the soil is more often tilled, which favors DOC formation to a higher extent than under grassland superiority (Osiny 1) [7, 8, 13].

Hydrology and temperature could also play an important role in both production and mobilization of DOC in the studied agricultural soils. DOC outflow from the drained sites was similar for all sampling time, except for the peaks in concentration that coincided with high rainfall (summer 1999), which were most pronounced for sites with high doses of manure (Table 1). The formation of water-soluble organic materials could be increased through the positive influence of moisture and temperature on microbial activity, DOC deposition (rainfall in the temperate zone contains dissolved organic carbon concentrations in the range of 0.82–2.00 mg C dm^{-3}) or through the rewetting effect after dry periods (the greater draw down of water tables in summer, increasing the depth of the oxidation zone and production of DOC; a rising water table, that intersects high DOC concentrations in the upper soil layer, enlarges vertical transport of DOC) [8, 14–16].

Water percolating through soil surface horizons is considerably enriched in DOC, but then other factors control whether these high DOC concentrations actually reach the ground or surface waters. Encapsulation of OM, flocculation of clay particles, adsorption of mineral particles around organic particles, or stable aggregate formation as well as promoting water retention will reduce DOC leaching [1, 2, 8, 17]. The degree of interaction between soils and waters depends on the soil properties, such as pH or phosphorus content. It is known that the sorption capacities of several mineral phases for organic matter increase with decreasing P content and pH [18, 19]. This seems to explain the comparatively low concentration of DOC in waters from watersheds Majdan

1–3, intensively fertilized and characterized by the soil with a high (41.66 %) percentage of particles with a diameter below 0.02 mm, very low content of phosphorus and pH < 4.5 (Table 3).

The effect of pH values on DOC content in the soils sampled from the studied sites, was also noticed in the laboratory experiment (Table 4). Although a significant correlation between H^+ and DOC concentrations was not observed, which, according to Pietri and Brookes [20], might have been connected with different origin of analyzed soils, an increase in pH above 7.0 or decrease below 4.0 resulted in the dissolution of organic matter (Table 4). Higher solubility of organic matter in alkaline soils is attributed to increased deprotonation of the hydroxyl groups and a change in the microbial community, whereas in acidic soils the dissolution of organic complexes containing polyvalent cations and the advancing saturation of exchange sites are the main factors elevating DOC contents [2, 5, 19].

Table 4

DOC concentrations [mg kg^{-1}] in soils

Area	pH						$\overline{X}$
	3.5	4	5	6	7	7.5	
Osiny	65.78	58.25	54.93	57.93	81.75	99.80	69.74
Ownia	59.63	50.88	47.70	48.28	59.82	54.88	53.53
Majdan	66.10	60.13	40.80	38.68	47.13	71.83	54.11
Zalesie	79.68	64.93	69.23	84.65	98.35	103.60	83.40
$\overline{X}$	67.79	58.54	53.16	57.38	71.76	82.53	65.20

$LSD_{0.05}$ for areas (1) – 10.87; for pH (2) – 14.80; for 1 × 2 – 37.29

Conclusions

The experiments showed that biotic and abiotic factors are likely to control the dynamics of dissolved organic carbon in analyzed drainage waters. It seems that the increase in DOC concentrations in water draining from watersheds is dependent mainly on the over-application of FYM and NPK fertilizers, rise in rainfall and temperature, as well as properties of the soil (percentage of particles with a diameter below 0.02 mm, content of phosphorus and pH). It was found that in both acidic and alkaline soils DOC leaching is liable to increase. However, there do not appear to have been any regular trends in chemical and environmental factors, soil management or land use affecting all analyzed watersheds. Therefore, the influence of them on DOC concentration may be difficult to predict under field conditions.

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ZAWARTOŚĆ ROZPUSZCZALNEGO WĘGLA ORGANICZNEGO W WODACH DRENARSKICH I GLEBACH Z EKOSYSTEMÓW ROLNICZYCH

Katedra Chemii Rolnej i Środowiskowej, Uniwersytet Przyrodniczy w Lublinie

Abstrakt: Celem przeprowadzonego dwuletniego doświadczenia polowego i laboratoryjnego było zbadanie wpływu użytkowania gleby, użytkowania gruntów, warunków klimatycznych i właściwości gleb na zawartość rozpuszczalnego węgla organicznego (DOC) w wodach drenarskich i glebach. W doświadczeniu polowym pobierano wody drenarskie z 12 działów drenarskich (w każdym z czterech obszarów badawczych, charakteryzujących się zróżnicowanymi właściwościami glebowymi, wytypowano po trzy obiekty badawcze – działy drenarskie, zlokalizowane na zróżnicowanych pod względem użytkowaniu gruntów i zabiegów agrotechnicznych terenach). W doświadczeniu laboratoryjnym w glebach pobranych z czterech obszarów badawczych symulowano wartości pH typowe dla polskich gleb i oznaczano zawartość DOC. Stwierdzono, że zawartość DOC może się zwiększać w wyniku stosowania obornika i nawozów NPK, wzrostu temperatury i opadów (podczas lata), jak również jest uzależniona od właściwości gleby (udziału frakcji o średnicy 0,02 mm, zawartości fosforu oraz pH). Jednak w warunkach polowych wpływ poszczególnych czynników na zawartość DOC może być trudny do przewidzenia z uwagi na ich nakładanie się.

Słowa kluczowe: DOC (rozpuszczalny węgiel organiczny), wody drenarskie, użytkowanie gleby, właściwości gleby

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Elżbieta SROKA[1]

HYDROCHEMISTRY OF THE LAKE ŚWIDWIE (WATER-MARSHES BIRD RESERVE) IN 2004

HYDROCHEMIA JEZIORA ŚWIDWIE (REZERWAT PTACTWA WODNO-BŁOTNEGO) W 2004 R.

Abstract: "Jezioro Świdwie" Reserve is an exceptional wetland and marshland area of international importance and it was as one of five Polish reserves that was listed in the "Ramsar" International Convention. Świdwie Lake research was conducted in 2004 in: spring, summer, and autumn. Chemical analysis included basic water quality indicators, such as: dissolved oxygen, perc cent oxygen saturation, organic matter content (BOD_5, COD_{Cr}), nutrient contents and extent of mineralization (Cl, SO_4).

Keywords: Lake Świdwie, hydrochemical conditions, nutrients

Świdwie Lake is an ornithological nature reserve located approximately 20 km to the West from Szczecin within the borders of Police and Dobra districts. It was established in 1963, spreading over an area of 382 ha and enlarged to 891,28 ha in 1988. It encompasses Świdwie Lake along with the rushes, meadows, peat land and forest belt surrounding the lake. The combination of a shallow water area with vast aquatic and waterside vegetation creates exceptionally favourable breeding conditions for water birds and mud birds. There are approximately 240 species nesting within the reserve. In 1984 the reserve was entered into the list of the "Ramsar" Convention on Wetlands [1].

Świdwie Lake is a shallow, strongly eutrophicated water area, largely overgrown with bulrush and reed, which divides the water surface into two separate water areas of the approximate size 50 ha and 26 ha. Currently the maximum depth of the larger water area is 2.4 m, average depth 0.7 m, and its maximum length 157 m [2, 3]. The aim of the research was to define current hydrochemical conditions of Świdwie Lake.

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[1] Department of Marine Ecology and Environmental Protection, Szczecin University of Agriculture, ul. Kazimierza Królewicza 4D, 71–550 Szczecin, email: elzbieta.sroka@fish.ar.szczecin.pl

Material and methods

Świdwie Lake research was conducted in 2004 at 5 sites: 1 – N53^{o}33.490′; EO14^{o}22.665′, 2 – N53^{o}33.573′; EO14^{o}22.411′, 3 – N53^{o}33.659′; EO14^{o}22.279′, 4 – N53^{o}33.592′; EO14^{o}21.891′, 5 – N53^{o}33.330′, N53^{o}33.330′; EO14^{o}22.544′ (Fig. 1).

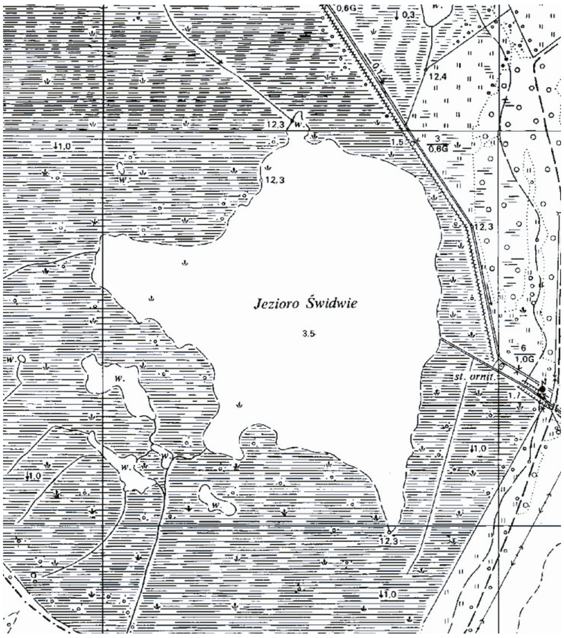

Fig. 1. Locations of sampling sites on Lake Świdwie

At sites 1, 3, 4, 5 water samples were taken from near-surface layer (0.5 m), whereas at station 2 from near-surface layer (0.5 m), as well as from near-bottom layer (0.5 m above the bottom) using Ruttner water bottle. Sampling was performed on days allowing to observe changes that are characteristic for particular climatic seasons (23.03.2004, 04.06.2004, 13.07.2004, 05.10.2004 and 24.11.2004).

Hydrochemical analysis included basic water quality indicators such as: dissolved oxygen, per cent oxygen saturation, organic matter content (BOD_5, COD_{Cr}), nutrient contents and extent of mineralization. Chemical laboratory analysis was conducted in accordance with the Standard Methods recommended by the State Inspectorate for Environmental Protection for lake waters analysis [4, 5]

Results

Świdwie Lake waters were overoxygenated during spring and summer (100.2––112.4 % O_2) at sites 1, 2, 5 and underoxygenated during autumn (76.7–96.2 % O_2) at all sites. The worst oxygen conditions in the course of the entire research period were

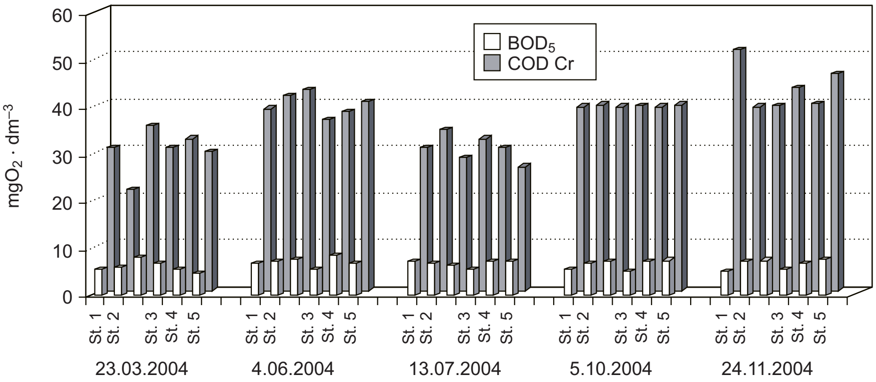

Fig. 2. Organic matter load in Lake Świdwie water

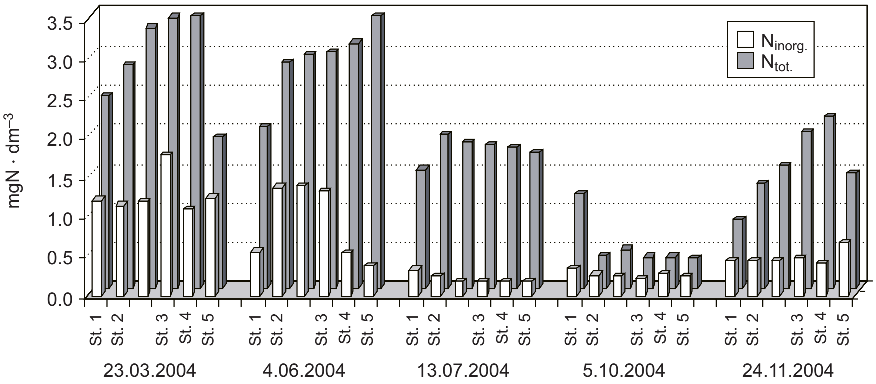

Fig. 3. Variability of inorganic nitrogen and total nitrogen contents in the Lake Świdwie water

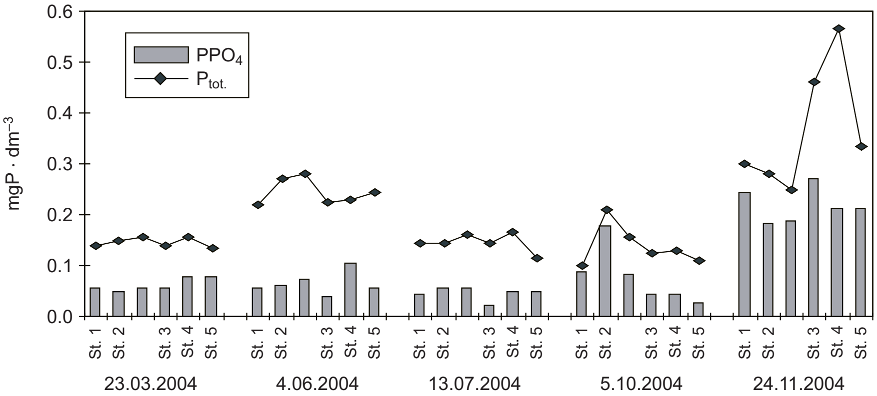

Fig. 4. Seasonal variability of orthophosphate and total phosphorus contents in water of Lake Świdwie

noted in the near of site 3 (76.7–84.1 % O_2). The factors characterizing total organic material content in water (BOD_5, COD_{Cr}) had the values from 5.0 to 8.5 $mgO_2 \cdot dm^{-3}$ and from 21.6 to 51.2 mg $O_2 \cdot dm^{-3}$. Site 2 was the most loaded with organic material (Fig. 2). The concentration of phosphate phosphorus was within the range of 0.022–0.245 mg $PPO_4 \cdot dm^{-3}$. Whereas the concentration of total phosphorus was from 0.1 to 0.565 mg $P_{tot.} \cdot dm^{-3}$ (Fig. 4). Mineral nitrogen concentration was within the range of 0.174–1.178 $mgN_{inorg.} \cdot dm^{-3}$ and the dominant form was nitrate nitrogen. The values determined for total nitrogen concentration oscillated between 0.372–3.453 mg $N_{tot.}$ x dm^{-3} (Fig. 3). The values determined for chlorides and sulphates in the waters of the water region researched amounted to respectively: 28.4–71.0 mg $Cl^- \cdot dm^{-3}$ and 13.33–49.52 mg $SO_4^{2-} \cdot dm^{-3}$.

The results of hydrochemical analysis enabled to evaluate the current state of the water quality in the lake under discussion.

Water oxygenation in percentage values is a coefficient of the intensity of assimilation and dissimilation processes taking place in natural waters. If processes of photosynthesis predominate in a water basin, then the waters are overoxygenated, but if dissimilation processes predominate, the waters are underoxygenated [6, 7].

Świdwie Lake waters were overoxygenated in the spring and summer seasons and underoxygenated in the autumn season. This phenomena is characteristic for water basins with high trophy. Also, high organic material load and high phosphorus compounds concentrations are typical for fertile lakes and they qualify this water region to class III of water purity [4, 8]. Mineral nitrogen concentration and total nitrogen concentration are within the range stipulated for class II of water purity and waters unclassified [4]. The degree of mineralization of the analyzed waters was characteristic for the lakes of Western Pomerania [9].

Świdwie Lake is a non-stratified, polymictic water region, which is indicated by: lack of temperature gradient in the summer season and small maximum depth. It has unfavourable morphological and morphometric conditions, which makes it vulnerable to degradation (III water purity class, III vulnerability class) [4].

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HYDROCHEMIA JEZIORA ŚWIDWIE (REZERWAT PTACTWA WODNO-BŁOTNEGO) W 2004 R.

Katedra Ekologii Morza i Ochrony Środowiska,
Akademia Rolnicza w Szczecinie

Abstrakt: Rezerwat „Jezioro Świdwie” to wyjątkowy obszar wodno-błotny o międzynarodowym znaczeniu, jako jeden z pięciu polskich rezerwatów ujęty w Międzynarodowej Konwencji „Ramsar”. Badania Jeziora Świdwie prowadzono w 2004 r. na 5 stanowiskach w sezonach wiosennym, letnim i jesiennym. Badania hydrochemiczne obejmowały następujące wskaźniki jakości wody: tlen rozpuszczony, procentowe nasycenie wody tlenem, zawartość materii organicznej (BZT$_5$, ChZT$_{Cr}$), stężenie biogenów i stopień mineralizacji.

Słowa kluczowe: Jezioro Świdwie, warunki hydrochemiczne, biogeny

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Bogdan SZOSTAK[1]

CONTENT OF SELECTED HEAVY METALS IN SOIL IN VARIOUS AREAS OF THE SWINE FARM

ZAWARTOŚĆ WYBRANYCH METALI CIĘŻKICH W GLEBIE Z RÓŻNYCH MIEJSC FERMY ŚWIŃ

Abstract: Heavy metals are present not only in the highly industrialized regions, but also in natural ecosystems and farm lands. Since the productivity of farm animals increases, more and more microelements are added to the feed, which may cause their excessive accumulation in the environment. Therefore, research was undertaken to determine the degree of soil contamination with heavy metals in various areas on a swine farm. The samples for tests were collected from the following places: the swine yard and at the distance of 4 metres from the yard fence, the dung plate – at the distance of 5 and 10 m, and the fattening house – at the distance of 20 m. The samples for analysis were taken in spring from the surface layer of the soil: 0–20 cm.

The content of lead and manganese in soil in various areas of the swine farm was within the limits qualifying the soil for the zero degree contamination. The highest concentration of zinc characterized the soil in the swine yard 141.8 mg · kg^{-1}), which qualifies the soil for the first degree of contamination. In the other areas, the content of zinc was within the limits characteristic of the zero degree contamination.

When the droppings are managed rationally, swine farms do not constitute any significant danger for the soil environment.

Keywords: heavy metals, soil, swine farms

Heavy metals are not only present in highly industrialised regions, but also in natural ecosystems and in those used agriculturally [1–3]. The extent of heavy metal contamination of soil depends on many factors, among others – on the type of land use [4]. The farmyards where swines are bred can, in some way, be sources of natural environment contamination. The problem itself is important, as in Poland over 1 million farms breed swine. In the environment of animals, heavy metals can be present in the atmospheric air, drinkable water and in soil, which animals may absorb either directly or indirectly with feed or plants [5]. Trace elements in the form of inorganic salt and oxides are added to farm animal feed. Microelements from these mixtures are characterised by low nutrient availability [6]. Higher and higher productivity of farm animals requires that high amounts of microelements should be added to feed, which

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[1] Faculty of Agricultural Science in Zamość, University of Life Science in Lublin, ul. Szczebrzeska 102, 22–400 Zamość, email: bszostak@wnr.edu.pl

may exceed the necessities of the animals, which in consequence leads to excessive accumulation of these microelements in the environment [7, 8].

Most of the research done so far was concerned with the effect of animal droppings on croplands contamination. Little research has been done concerning the problem of heavy metal soil contamination on swine farms. Therefore, research has been undertaken to estimate the degree of soil contamination with selected heavy metals at various farm objects characteristic of swine breeding.

Material and methods

The examined soil was collected from a swine farm situated in Tomaszów County of Lublin Province. The analysed farm produced about 5000 fattening pigs a year. The animals were kept on thin bedding. The manure was removed from the farm everyday and accumulated on the dung plates, situated near the pig houses. The soil samples were taken from the surroundings of the following farm objects: the sow yard, about 4 m from the yard fence, the dung plate – at the distance of 5 and 10 m and the fattening house – at the distance of 20 m. The samples for analyses were gathered in spring from the surface layer of soil: 0–20 cm.

In the analysed soil samples, the contents of general forms of lead, zinc and manganese were determined. The soil samples underwent hot mineralization in concentrated nitric(V) acid and chloric(VII) (perchloric) acid, and then the content of analysed metals was established using the method of atomic absorption spectrometry.

The results of the analyses were compared with the limit contents of heavy metals established by IUNG [9] and limit numbers for metals in selected countries of the European Union.

Results and discussion

The minimum, maximum and average contents of lead in soil collected at various farm objects on a swine farm are shown in Table 1. The highest content of lead was

Table 1

The content of the total lead in analysed farm soil [mg · kg^{-1}]

Object	Content Pb [mg · kg^{-1}]		
	min.	max	average
Sows yard	17.0	23.5	19.7
4 m from the yard fence	31.5	32.0	31.8
Dung plate 5 m	27.5	29.5	28.8
Dung plate 10 m	20.0	21.5	20.7
Fattening house 20 m	11.5	15.5	14.0
Average			23.0

noted in soil collected from the layer of 0–20 cm at the distance of 4 m from the fence of the swine yard. The average content of lead in this area was 31.8 mg · kg^{-1}) and the maximum – 32.0. Literature gives various values of geochemical background for lead in soils. The natural content of lead in the Polish soils is 8–25 mg/kg, and the admissible value is 50–100 mg, depending on the type of soil [5]. The contents of lead established by us should be treated as natural because they are within the zero degree soil contamination with heavy metals, according to the IUNG scale designed by Kabata-Pendias et al [9]. The limit numbers defining the zero degree lead soil contamination in selected countries of the European Union (England, Holland, France, Germany) are also higher than those estimated in the soil on the analysed farm [4].

Table 2 shows minimum, maximum and average contents of zinc in soil at various objects on a swine farm. The highest average concentration of zinc was determined in the soil collected from the swine yard (141.8 mg · kg^{-1}). The maximum content of zinc in soil samples collected in this area was 148.0 mg · kg^{-1}. According to the classification designed by Kabata-Pendias' team [9], the zinc concentration established by us, in the soil characterized by high content of organic matter (> 10 %) on a swine farm, qualifies the soil for the zero degree contamination with heavy metals. Terelak et al [10] state that the natural contents of zinc in cropland soil in Poland are within 0.5–100.0 mg · kg^{-1}. The authors found that the highest areas of such soils are, among others, in the Lublin Province. The limits of zinc content in soil are too high for the human health, and in many EU countries are much higher than in Poland [4]. However, the substantial toxicity of the element to living organisms and the easiness with which it enters food chains explains why ecologists and toxicologists are so much interested in the occurrence of this element in the natural environment.

Table 2

The content of total the zinc in analysed farm soil [mg · kg^{-1}]

Object	Content Zn [mg · kg^{-1}]		
	min.	max	average
Sows yard	137.0	148.0	141.8
4 m from the yard fence	22.5	30.5	27.7
Dung plate 5 m	48.5	53.5	51.3
Dung plate 10 m	31.5	34.0	32.3
Fattening house 20 m	26.0	27.0	26.7
Average			56.0

The manganese concentration in swine farm soil is shown in Table 3. The highest concentration of manganese has been found in the soil collected at the distance of 5 m from the dung plate. The average content of this element was 368.8 mg · kg^{-1}, and the maximum content of manganese in soil samples collected from the above enumerated area was 391.5 mg · kg^{-1}. High average contents of manganese were found in soil collected from the swine yard (260.3 · kg^{-1}), at the area situated at the distance of 20 m from the fattening house (221.8 mg · kg^{-1}), and in the other analysed areas (> 200 mg · kg^{-1}). The general content of manganese in soils is most often within 100–1000

Table 3

The content of total the manganese in analysed farm soil [mg · kg^{-1}]

Object	Content Mn [mg · kg^{-1}]		
	min.	max	average
Sows yard	252.0	270.0	260.3
4 m from the yard fence	212.5	222.0	218.3
Dung plate 5 m	352.0	391.5	368.8
Dung plate 10 m	192.0	227.0	203.8
Fattening house 20 m	206.5	252.0	221.8
Average			254.6

mg · kg^{-1} [11]. The main source of manganese flow into the soil is rain waters [12], and in our case, an additional source of manganese flow was liquid manure and manure water from swine droppings. Mazur [13] claims that with liquid manure much more manganese enters soil in comparison to manure. Manganese soil contamination is connected with its form and not quantity [14]. The authors claim that excessive quantities of easily dissolving manganese can appear in soils fertilized with manure, which often contains its higher concentration as a result of using mineral additives in feed.

Conclusions

1. In swine farm soil, a natural content of lead was found. Soil samples collected at the distance of 4 m from the swine yard were characterized by the highest concentration of this element; the maximum content was – 31.8 mg · kg^{-1}.
2. The highest concentration of zinc was determined in the soil of the swine yard (141.8 mg · kg^{-1}), which qualifies the soil as being characterized by the zero degree contamination. The content of zinc at the other farm areas was within the limits specified for the zero degree contamination.
3. The average content of manganese in soil samples collected at various farm objects was between 203.8 to 368.8 mg · kg^{-1}. The highest concentration of manganese was determined in the soil samples collected in the area situated at 5 m from the dung plate.
4. When swine droppings are managed rationally, swine farms do not constitute any significant danger of contamination with heavy metals for soil environment.

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ZAWARTOŚĆ WYBRANYCH METALI CIĘŻKICH W GLEBIE Z RÓŻNYCH MIEJSC FERMY ŚWIŃ

Wydział Nauk Rolniczych w Zamościu,
Uniwersytet Przyrodniczy w Lublinie

Abstrakt: Obecność metali ciężkich stwierdza się nie tylko w rejonach silnego uprzemysłowienia, ale także w ekosystemach naturalnych i rolniczo wykorzystywanych. Coraz większa produkcyjność zwierząt gospodarskich wymaga stosowania dodatku mikroelementów do pasz w znacznych ilościach, które mogą przekraczać zapotrzebowanie zwierząt, konsekwencją czego może być zbyt duża ich akumulacja w środowisku. W związku z tym podjęto badania, mające na celu określenie stopnia zanieczyszczenia gleby wybranymi metalami ciężkimi przy różnych obiektach fermowych, które towarzyszą hodowli świń. Próbki do badań pobierano wokół następujących obiektów: wybieg dla loch i w odległości 4 m od ogrodzenia wybiegu, płyta gnojowa – w odległości 5 i 10 m oraz tuczarnia – w odległości 20 m. Próbki do analiz pobierano w okresie wiosennym z wierzchniej warstwy gleby: 0–20 cm.

Zawartość ołowiu i manganu w glebie przy różnych obiektach fermowych była w granicach kwalifikujących glebę do zerowego stopnia zanieczyszczenia. Największe stężenie Zn odnotowano w glebie na wybiegu dla loch (141,8 mg · kg), co kwalifikuje ją do pierwszego stopnia zanieczyszczenia. Przy pozostałych obiektach fermowych zawartość cynku w glebie mieściła się w granicach wyznaczonych dla zerowego stopnia zanieczyszczenia.

Słowa kluczowe: metale ciężkie, gleba, fermy świń

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Paweł WĘGOREK[1], Dariusz DROŻDŻYŃSKI[1],
Marek MRÓWCZYŃSKI[1] and Joanna ZAMOJSKA[1]

DYNAMICS OF ACETAMIPRID DISAPPEARANCE IN OILSEED RAPE PLANT TISSUES IN CONNECTION WITH ITS TOXIC ACTION AGAINST POLLEN BEETLE (*Meligethes seneus* F.) AND ITS INFLUENCE ON ECOLOGICAL ASPECT OF OILSEED RAPE CHEMICAL PROTECTION

DYNAMIKA ZANIKANIA ACETAMIPRYDU W TKANKACH ROŚLIN RZEPAKU OZIMEGO ORAZ JEGO TOKSYCZNOŚĆ DLA SŁODYSZKA RZEPAKOWEGO (*Meligethes aeneus* F.). ASPEKT EKOLOGICZNY OMAWIANYCH ZJAWISK

Abstract: Acetamiprid is a neurotoxine belonging to the neonicotinoid group. This active substance has contact and stomach action and acts on the insect central nervous system as agonist of the acetylocholine in nicotinic acetylocholine receptors. Acetamiprid has translaminar and systemic proprieties in plants and nowadays is one of the most widely used insecticides against pollen beetle (*Meligethes aeneus* F.) in Poland as a component of a commercial product Mospilan 20 SP. Constant and strong selective pressure of insecticides resulted in resistance of pollen beetle (PB) to many active substances used in Poland. It also influences beneficial fauna especially pollinators. The aim of the study was to determine the effectiveness of acetamiprid against pollen beetle in the period of 15 days that is characterized by rapid elongation of oilseed rape plants. The dynamics of mortal action of acetamiprid against pollen beetle and disappearance of acetamiprid in plant tissues were determined. Short analysis of acetamiprid potential toxic action against pollinators, especially against honeybee (*Apis mellifera* L.), predators and parasitoids was made.

Keywords: acetamiprid, pollen beetle, oilseed rape, systemic mode of action, pollinators' protection

Pollen beetle (PB) is the most dangerous pest of oilseed rape in Poland and in Europe. The pest has developed resistance against most synthetic pyrethroid and organophosphorous insecticides [1–6]. Acetamiprid was introduced against pollen

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[1] Institute of Plant Protection, National Research Institute, ul. Władysława Węgorka 20, 60–318 Poznań, email: wegorek.zamoyska@onet.eu

beetle in Poland in 1996 as a new active substance belonging to the neonicotinoid group [7], and has become a component of PB insecticide resistance management strategy. In last years a lot of signals on the decrease of acetamiprid effectiveness in PB control were reported from some regions of oilseed rape cultivations in Poland. Bioassays of acetamiprid for resistance monitoring have been performed in the Institute of Plant Protection in Poznań since 2004. The research demonstrated some level of resistance of PB to this active substance [4, 8, 9]. One of important factors influencing survival of insects is active substance concentration and penetration in plant and insect organism. The question: "what happens to acetamiprid molecules after their application in the oilseed plants", is worth of interest because of several aspects. The main one is beneficial fauna protection, that is, in case of oilseed rape, very important. It is also important to work out new effective strategies of pest control based on integrated resistance management programs to prevent PB resistance. And prevention of resistance phenomenon is closely connected with environment protection.

Material and methods

Chemicals and reagents

Acetamiprid – commercial product – Mospilan 20 SP – (200 g of acetamiprid/kg of product) was used. Recommended field concentration (120 ppm) of active substance was calculated assuming that the highest field dose in Poland is 0.12 kg of Mospilan 20 SP/ha/200 dm^3 of water .

Acetonitrile (gradient grade) was purchased from Labscan (Dublin, Ireland). Anhydrous magnesium sulphate (reagent grade), sodium citrate tribasic dihydrate (ACS reagent), and disodium hydrogen citrate sesquihydrate (pure) were all purchased from Sigma–Aldrich (Steinheim, Germany). Sodium chloride was purchased from POCH (Gliwice, Poland), Bondesil PSA bulk sorbent was purchased from Candela (Warsaw, Poland) and Supelclean ENVI-Carb from Supelco (Bellefonte, USA). Formic acid (ACS grade) was purchased from Merck (Darmstadt, Germany). Distilled deionized water was obtained using a Millipore Elix 3 system (Millipore, Billerica, USA). Nitrogen (purity 99.995 %) and argon (purity 99.9998 %) were supplied by Air Products Company, Poland. Certified pesticide standards of acetamiprid and simazine-D10 were purchased from Dr. Ehrenstorfer (Ausburg, Germany) and were of purity above 98.5 %.

Biological material

Pollen beetles from untreated oilseed rape field were collected for testing from the population of Winna Góra. Insects were placed into insulators made of airy material and filled with rape plants and transported to the laboratory. In the laboratory insects were kept for 24 hours at the temperature 10 ^{o}C (climatic chamber).

Oilseed plants were grown in pots of 25 cm diameter and 5 dm^3 volume in natural conditions. In the vegetative phase BBCH 45 (Bundesanstalt Budessortenamt und

Chemical Industry) oilseed plants were sprayed with demineralized water dilution of Mospilan 20 SP using hand sprayer (acetamiprid concentration was 120 ppm). Control plants were sprayed with demineralized water. Sprayed plants were collected 24, 120, 240 and 360 hours after treatement and used for PB mortality tests and for acetamiprid residue determination.

Laboratory tests

For determination of insect mortality 24, 120, 240 and 360 hours after treatment and lethal concentrations LC50 and LC95, a standard method recommended by Insecticide Resistance Action Committee (IRAC method no. 7) was used. The initial concentration of acetamiprid in demineralized water in laboratory tests was 240 ppm. The following 5 concentrations: 144, 86.4, 51.84, 31.1 and 18.66 ppm were used. Oilseed rape plants were dipped in each concentration of acetamiprid for about 5 seconds, then placed on a paper towel to dry for 3 hours in laboratory conditions (20–22 ^{o}C, photoperiod of 16:8 (L:D). Control plants were dipped in demineralized water. Dry treated plant material was placed into 0.9 dm^3 jars of 10 cm diameter filter paper lining their bottom. Length of plant material was of height of a jar (15 cm) and weight was 20 g. One hundred of PB beetles were placed in each jar. The jars were closed with airy material for ensuring a good evaporation and ventilation. Each dose was represented by three replications and a single control. A final assessment (lethal effect of acetamiprid) was determined after 24 hours and expressed as per cent mortality of insects at each dose in relation to untreated control.

For LC 50 and LC 95 calculations (expressed in ppm of acetamiprid) – computer program POLO PC was used. The program is based on Finney probit analysis method [10].

Sample preparation procedure

A portion of finely ground subsample was placed in a polypropylene centrifuge tube and water was added. Later, an internal standard solution (IS simazine-D10) and acetonitrile were added and the sample was extracted using Ultra-Turrax homogenizer. Further, disodium hydrogen citrate sesquehydrate, trisodium citrate dihydrate, anhydrous magnesium sulphate and sodium chloride were added, and the mixture was immediately hand-shaken, then centrifuged. Afterwards, aliquot portion of the supernatant was transferred to a polypropylene centrifuge tube containing of cleanup mixture (anhydrous magnesium sulphate, ENVI-Carb and PSA). The tube was vortexed and centrifuged. An aliquot portion of the supernatant was transferred into a glass test tube and the extract was evaporated to dryness under a stream of nitrogen and the residue was re-dissolved in mixture of 0.1 % formic acid in methanol and 0.1 % formic acid in water prior to its injection into the LC–MS/MS system.

Chromatographic conditions

An ACQUITY UPLC ultra-performance liquid chromatograph system (Waters, USA) with a column and autosampler thermostats equipped with a tandem quadrupole mass spectrometer (Waters Quattro PremierXE) was operated using MassLynx software [11]. Waters ACQUITY UPLC column (BEH C18 2.1 × 100 mm, 1.7 μm) was used for final LC analysis. Temperature of the column and autosampler thermostats was 30 ^{o}C. 5 mm^3 samples were injected into the system. Then, the column was eluted with the mobile phase: water with 0.1 % formic acid (A) and methanol with 0.1 % formic acid (B) at the flow rate of 0.3 cm^3/min using gradient mode.

MS/MS conditions: Typical interface conditions for maximum intensity of the precursor ions were optimized as follows: nebulizer and desolvation (drying gas) N2 flows were set at 100 and 700 dm^3/h, respectively, source block and desolvation temperatures were 120 and 350 ^{o}C, respectively.

Argon was used as a collision gas at the pressure of 6.9 × 10.3 mbar. Selection and tuning of MRM transitions were performed individually for acetamiprid and simazine-D10. Both compounds were analyzed using a positive electrospray ionization mode (ESI+).

Acetamiprid MS/MS parameters: Cone: 35 V, Ion Transition 1: 223 > 126, Collision Energy 1: 20 eV, Ion Transition 2: 223 > 90, Collision Energy 2: 30 eV

Simazine-D10 MS/MS parameters: Cone: 35 V, Ion Transition: 212 > 137, Collision Energy: 20 eV

The second acetamiprid transition was used for qualitative determination of target compound. Retention time of acetamiprid was 1.68 min. The limit of quantification of acetamiprid was determined at 0.01 mg/kg.

Validation of the method

All validation procedures were performed using control samples of oilseed rape plant. Recoveries were determined for five replicate determinations at two spiking concentrations: 0.01 and 0.1 mg/kg. Precision was expressed as relative standard deviation (RSD) at each spiking level (5 samples spiked at each level). Linearity of the method for determination of acetamiprid was assessed by multilevel standard calibration curves (from 0.01 μg/cm^3 to 0.5 μg/cm^3, $R^2 = 0.9948$). The samples of oilseed rape plant spiked with acetamiprid were extracted applying the method described above. Analytical standard signal was compared with the signal of the control sample extract spiked with the target compound before the whole procedure. Average residues of acetamiprid were 90.16 ± 15.55 % at the level 0.01 mg/kg and 93.32 ± 11.73 % at the level 0.1 mg/kg.

Results and discussion

Results shown in Table 1 indicate quick decline of PB mortality with the increase of time after spraying oilseed rape plants with Mospilan 20 SP. Survival of 80 % of beetles 120 hours after treatment with the recommended concentration of acetamiprid indicates some level of resistance to acetamiprid of examined pest population.

Table 1

Mortality of pollen beetle after contact
with oilseed rape plants treated with Mospilan 20 SP

Hours after treatment	Mortality [%]
24	92
120	20
240	15
360	5

Results presented in Table 2 show that one day after treatment mean LC50 concentration for the tested PB population was 29.6 ppm and mean LC95 value was 340.6 ppm.

Table 2

Lethal concentrations of acetamiprid for pollen beetle expressed as LC50 and LC95, in ppm

Lethal concentration	Date of testing			Mean
	25.04.2008	30.05.2008	17.06.2008	
LC50 (confidence intervals)	24 (9.32–38.04)	37 (21.8–50.4)	28 (17.2–38.9)	29.6
LC95	342	258	422	340.6

Results shown in Table 3 and Figure 1 confirm the conclusion that satisfactory effect of acetamiprid systemic action against pollen beetle is short and, in practical conditions, may be too weak to control resistant populations of this pest during the period longer than a few (2–3) days.

Table 3

Acetamiprid contents in oilseed plant tissues after treatment with Mospilan 20 SP, in ppm

Hours after treatment	Sample 1	Sample 2	Sample 3	Mean
	[ppm]			
24	44.26	41.60	39.81	41.89
120	4.46	4.28	4.31	4.35
240	1.77	1.91	1.89	1.86
360	0.49	0.55	0.59	0.54

Dependently on population density, in field conditions, the satisfactory effect of insecticide action should be on the level of 70–85 % mortality of beetles. The research show that the level of active substance concentration enabling the achievement of this level, is too low and unsatisfactory 2–3 days after oilseed rape plants treatment. So, systemic action of acetamiprid in oilseed rape plants seems to be too weak. It can be caused by rapid plant elongation. This phenomenon probably causes diluting of the active substance in plant tissues and decreases of acetamiprid content on the leaves' surface to the level, which is tolerated by PB. In Polish climatic conditions PB attack is

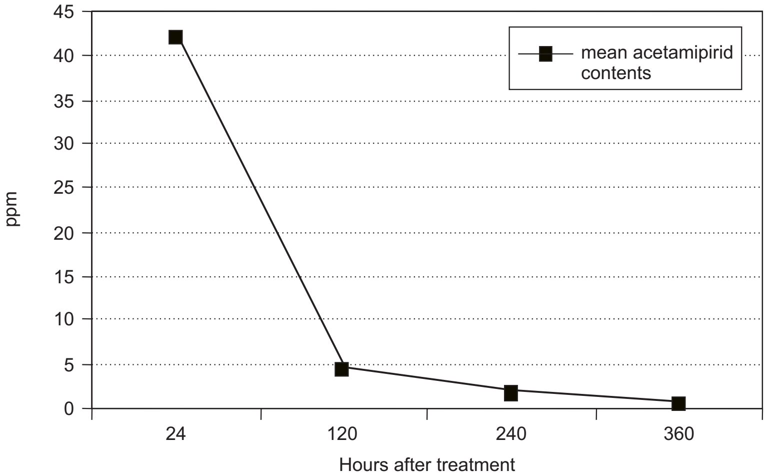

Fig. 1. Dynamics of acetamiprid disappearance in oilseed rape plant tissues treated with Mospilan 20 SP

often strong, constant and prolonged in time. Results indicate that during the elongation period of oilseed rape plants and strong PB attack the chemical treatment with acetamiprid should be repeated 3–4 days after the first one.

In relation to beneficial fauna (*Apis mellifera, Coccinella septempunctata, Poecilus cupreus, Typhlodromus pyri* and *Aphidius rhopalosihpi),* when comparing results of experiments presented above (Table 1–3, Fig. 1) with data from the European Commission – Acetamiprid [12, 13] it can be stated that recommended concentration of acetamiprid in Poland (120 ppm or 0.24 μg/cm^2) can cause high initial mortality of *Aphidius rhopalosiphi,* because even 90 ppm of acetamiprid results in 53.1 % mortality of this species. It can be also toxic for *Typhlodromus pyri,* because 90 ppm of acetamiprid results in 51.7 % mortality of this species. In relation to *Poecilus cupreus* even such a high concentration as 1000–2000 ppm results in 3.3 % mortality of this species. The concentration 450 ppm causes 100 % mortality of *Coccinella septempunctata* larvae. The dose of 0.24 μg/cm^2 recommended in Poland, in relation to honeybee *Apis mellifera,* for which acute oral toxicity LC50 is 8.85 μg/bee and acute contact toxicity LC50 9.26 μg/bee, seems to be moderately toxic up to 24 hours after treatment. The dynamics of acetamiprid disappearance in oilseed plants' tissues is quick and this active substance does not cause much risk for the pollinators and other beneficial fauna of oilseed rape fields.

Conclusions

1. Acetamiprid is relatively save for honeybee and some insect species of oilseed rape fields in concentration recommended in Poland.

2. Pollen beetle is a pest insect species of high natural resistance to many natural and synthetic active substances. Tested population from Winna Góra demonstrated some level of tolerance to acetamiprid.

3. Rapid oilseed plant elongation reduces the systemic action of acetamiprid.
4. A widespread use of Mospilan 20 SP can lead to PB resistance level increase and control failure in practical conditions.
5. Migration and prolonged attack of PB on oilseed rape plants in connection with its resistance requires repeated plant protection chemical treatment against this pest.

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DYNAMIKA ZANIKANIA ACETAMIPRYDU W TKANKACH ROŚLIN RZEPAKU OZIMEGO ORAZ JEGO TOKSYCZNOŚĆ DLA SŁODYSZKA RZEPAKOWEGO (*Meligethes aeneus* F.). ASPEKT EKOLOGICZNY OMAWIANYCH ZJAWISK

Instytut Ochrony Roślin, Państwowy Instytut Badawczy

Abstrakt: Acetamipryd jest silną neurotoksyną należącą do chemicznej grupy neonikotynoidów wykorzystywaną szeroko w chemicznej ochronie roślin. Ta substancja aktywna działa na centralny system nerwowy owadów na drodze kontaktowej oraz żołądkowej. Jej molekularne działanie polega na agonistycznym, w stosunku do acetylocholiny, działaniu na postsynaptyczne receptory tego neurotransmitera. Acetamipryd ma właściwości przenikania do tkanek roślin i oddziaływania systemowego. Obecnie w Polsce należy on do najpopularniejszych insektycydów w zwalczaniu słodyszka rzepakowego (*Meligethes aeneus* F.) oraz wielu innych szkodników jako komponent środka ochrony roślin – Mospilan 20 SP. Trwający już ponad 50 lat stały nacisk selekcyjny chemicznymi środkami spowodował u słodyszka rzepakowego w Polsce narastanie zjawiska odporności na wiele substancji aktywnych. Acetamipryd wpływa również na faunę pożyteczną, głównie na owady zapylające. Celem pracy było określenie dynamiki zanikania acetamiprydu w tkankach roślin rzepaku ozimego w okresie 15 dni od zabiegu chemicznego w fazach szybkiego wzrostu roślin oraz równoległe zbadanie jego toksyczności w stosunku do słodyszka rzepakowego, który jest w tym okresie głównym szkodnikiem atakującym rzepak. Na podstawie uzyskanych wyników oraz danych dotyczących acetamiprydu zamieszczonych w badaniach toksykologicznych tej substancji chemicznej przeprowadzono analizę zagrożenia działania tego insektycydu dla owadów zapylających, a szczególnie dla pszczoły miodnej (*Apis melliera* L.), drapieżców i parazytoidów.

Słowa kluczowe: acetamipryd, słodyszek rzepakowy, rzepak ozimy, systemowy mechanizm działania, ochrona zapylaczy

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Mariola WRÓBEL[1], Justyna CHUDECKA[2],
Tomasz TOMASZEWICZ[2] and Małgorzata GAŁCZYŃSKA[3]

CONTENTS OF HEAVY METALS IN ROADSIDE SOILS AND SPATIAL DISTRIBUTION OF METALLOPHYTE PLANT SPECIES ON THE ROADSIDES OF SZCZECIN LOWLAND

ZAWARTOŚĆ METALI CIĘŻKICH W GLEBACH PRZYDROŻNYCH A PRZESTRZENNE ROZMIESZCZENIE GATUNKÓW METALOFITÓW NA POBOCZACH DRÓG NIZINY SZCZECIŃSKIEJ

Abstract: Research on soil pollution with heavy metals and roadside metallophyte plant species spatial distribution along public roads within forest and agricultural areas in Szczecin Lowland was carried out. The roadside zones of about 8 m total width were surveyed. The total content of Mn, Pb and Cu in field and forest roadside soil samples decreased in roadside zones as moving away from the road. However, in the zone of 2 m width the field roadside soil showed the accumulation higher level of the analysed heavy metals as compared with that of forest one, ie by about 25 % more of Pb and Mn and about 60 % more of Cu. Differences in the content of heavy metals in roadside soils depended on a zone distance from the road, the soil granulation and pH reaction. Analysis of spatial and quantitative distribution of metallophyte species against the background of zonal roadside structure confirmed obtained results concerning the presence of heavy metals in roadside soil samples.

Keywords: roadside flora, metallophyte species, heavy metals, polluted soils

Roadside flora as well as the soil and air in the vicinity of roads undergo contamination by oil derivatives and carbon, nitrogen and sulphur oxides as well as by toxic heavy metal compounds and elements contained in motor vehicle exhausts. Automobile exhaust emission is accompanied by deposition of dust on the roadway and roadside. This dust is produced as a result of wearing off the break lining, tyres, road

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[1] Department of Botany and Nature Protection, West Pomeranian Technological University, ul. J. Słowackiego 17, 71–434 Szczecin, email: mariola.wrobel@zut.edu.pl

[2] Department of Soil Erosion and Soil Reclamation, West Pomeranian Technological University, ul. Pawła VI 1, 71–441 Szczecin, email: erozja@zut.edu.pl

[3] Department of Chemistry, West Pomeranian Technological University, ul. J. Słowackiego 17, 71–434 Szczecin, email: malgorzata.galczynska@zut.edu.pl

surface and lacquered car body metal elements as well as due to carrying various cargos [1, 2]. Road dusts and motor vehicle exhausts contain first of all Zn, Cu, Pb, Cd and Mn but the roadside soil is contaminated the most by heavy metals. These chemical elements get into soil with dry deposition and rainwater, with their highest concentration being observed in the soil top, 0.2 m deep humus layer directly adjacent to the roadway as well as in the roadside zone of several meters width. The observable decrease of their content is found only at the distance of 50–100 m from the road [3–5].

Excessive amounts of heavy metals in soil lead to plant external damages, metabolic conversion disturbances and increased accumulation in plant organs. The largest amounts of these chemical elements are found in plant roots and overground vegetative parts, while the least ones in generative organs. The increased content of heavy metals in plant overground organs is a result of direct effect of dusts and automobile exhausts. On the other hand, heavy metals pervade the plant roots from the soil contaminated by these chemical elements. The overabundance of heavy metal ions induces a series of biochemical and physiological changes in plant cell, which are defined as the syndrome of features being characteristic for heavy metal-induced stress [6–9].

Material and methods

The aim of undertaken studies was evaluation of the road shoulder soil pollution with heavy metals and its influence on the presence of metallophyte species in roadside flora of forest and field roads. Field observations were carried out in 2006–2007 at 8 permanent study points located along forest and field public roads with hardened surface outside the built-up area (Szczecin Lowland). The field roads were running through the pastures, grasslands, arable and fallow lands whereas the forest ones were situated within timber forests of the Goleniow Primeval Forest. The location of each permanent study point was marked with GPS respectively for forest roads (L1: 53^{o}34′26″N, 014^{o}47′09″E; Λ2: 53^{o}33′03″N, 014^{o}36′32″E; L3: 53^{o}27′08″N, 014^{o}52′12″E; L4: 53^{o}27′08″N, 014^{o}52′12″E) and the field ones (P1: 53^{o}18′17″N, 014^{o}48′0″E; P2: 53^{o}07′26″N, 014^{o}47′14″E; P3: 53^{o}20′28″N, 014^{o}47′14″E; P4: 53^{o}20′07″N, 014^{o}51′41″E) [10].

In all eight permanent study points were delimited 3 parallel transects crossing the road shoulder and including succeeding roadside zones: A – road shoulder edge (0–0.3 m width), B – proper road shoulder (0.3–2 m), C – ditch (2–5 m) and D – slope (5–8 m). In the each zone of the transect a plot (1 m^2) was delimited where all occuring plant species and their participation in vegetation cover of the plot were noticed. The nomenclature of identified vascular plants was given after Rothmaler [11] and Mirek [12]. The plant species resistant to increased heavy metal content in the soil and defined as metallophyte species were distinguished basing on the Zarzycki's ecological index numbers [13].

Out of each of the eight permanent study points, cumulative soil samples from four separated roadside zones were collected. In total, 32 soil samples from the top humus layer of soil (0–0.1 m) were obtained. For the soil samples composition and reaction measured in KCl with a concentration of 1 mol · dm^{-3} (pH in KCl) were determined.

The total content of lead, copper and manganese was assayed with the AAS method, after previous mineralisation of soil material in chloric(VII) (perchloric) and nitric(V) acid mixture (1:1) in a ratio of 1:10 (soil : acid).

Results and discussion

Basing of the results of floristic observations carried out in designated study points in the Szczecin Lowland, the presence of plant species tolerating the increased content of heavy metals in soil was found in the roadside flora. From among 143 noticed plant species up to 21 metallophyte species were recognized (14.6 %). These species belonged to 10 families (with the most numerously represented was *Poaceae* family) and participated in floristic composition of plant communities growing up on roadsides (Table 1).

Table 1

Spatial distribution of roadside metallophyte plant species in following zones of forest and field roadsides in Szczecin Lowland

Family	Metallophyte plant species	Field roadsides zones				Forest roadsides zones			
		A	B	C	D	A	B	C	D
Equisetaceae	*Equisetum arvense* L.	+	+	+	+	–	+	–	–
Chenopodiaceae	*Atriplex patula* L.	–	–	+	–	–	–	–	–
Caryophyllaceae	*Cerastium arvense* L.	–	–	–	–	–	–	+	–
	Cerastium semidecandrum L.	+	+	–	–	+	+	–	–
Rosaceae	*Fragaria vesca* L.	–	–	–	–	–	–	–	+
	Rubus caesius L.	–	+	+	+	–	–	+	–
	Rubus idaeus L.	–	–	–	–	–	–	–	+
Fabaceae	*Lotus corniculatus* L.	–	+	+	+	–	–	–	–
Convolvulaceae	*Convolvulus arvensis* L.	+	+	+	+	+	+	–	–
Campanulaceae	*Campanula rotundifolia* L.	–	–	+	–	–	–	–	–
Asteraceae	*Bellis perennis* L.	+	+	–	–	–	–	–	–
	Cichorium intybus L.	+	+	–	–	+	–	–	–
	Leontodon autumnalis L.	+	+	–	–	+	+	–	–
Poaceae	*Arrhenatherum elatius* (L.) P. B. ex J. et Presl	+	+	+	+	+	+	–	–
	Calamagrostis epigejos (L.) Roth	+	+	+	+	–	+	+	+
	Festuca ovina L.	–	–	–	–	–	+	+	–
	Festuca pratensis Hudson	+	+	+	–	–	–	–	–
	Festuca rubra L.	–	–	–	–	–	+	–	–
	Lolium perenne L.	+	+	–	–	+	+	–	–
Cyperaceae	*Carex arenaria* L.	–	+	+	–	–	+	+	+
	Carex hirta L.	+	+	–	–	+	+	–	–
Total	21	11	14	10	6	7	11	5	4

A – road shoulder edge; B – proper road shoulder; C – ditch; D – slope

The only species *Leontodon autumnalis*, described in literature as requiring the increased content of heavy metals in soil, grew up in masses in the proper roadside zone being contaminated the most by traffic pollutants coming from automobile exhaust emissions [13].

Spatial analysis of the distribution of distinguished metallophyte species against the background of zonal roadside structure showed significant floristic differences between the roads coming through forest lands and those under arable cultivation. They result not only from different character of vegetation which occurs in the road surroundings but first of all from different soil conditions and differences in the content of heavy metals in the roadside soil of analysed road types.

In Table 2 are presented the properties of soils sampled in the study points, which affect the availability of heavy metals for plants, ie soil reaction and content of granulometric fraction size ∅ < 0.02 mm [14]. Soil samples from the field roadsides, with content of granulometric fraction size ∅ < 0.02 mm from 7 to 16 %, were included into very light and light soils. Soil samples from the forest roadsides were more uniform in respect of size composition, they all belong to very light soils (with content of the granulometric fraction size ∅ < 0.02 mm from 2 to 7 %). Analysis of the reaction (pH_{KCl}) of soil coming from the forest roadsides showed a large differentiation of that trait. The top layer of soil (0–0.1 m), within the A and B roadside zones (to 2 m width), had a neutral reaction that changed to strongly acidic one in further roadside zones and was submitted to the acidifying effect of forest communities (fresh coniferous forest), through which the road was passing. The field roadside soils were generally characterised by a neutral reaction, although an increasing trend in the pH value (to alkaline one) was visible in the A roadside zone (0–0.3 m width). It results from the use of road surface deicing agents in winter (mainly sodium and calcium chlorides) which partly accumulate in the roadside soil [10].

When evaluating the total content of Mn, Pb and Cu in field and forest roadside soil samples (Table 2), a clear trend was observed to decreasing their quantities as moving away from the road. It was more clearly defined in relation to lead and copper than manganese. According to the evaluation criteria for the total content of heavy metal ions proposed by Kabata-Pendias [15], and presented in the table 2, the exceedance of natural lead and copper concentration to the level defined as the "raised" one (Ist degree), takes place within the two-meter zone of these soils, directly adjacent to the road (A and B roadside zones). Only in one case the copper concentration was defined as medium-contaminated soil (IIIrd degree).

Mean lead quantity in A and B zone (0–2 m total width) of field roadside soil amounts to 41.4 $mg \cdot kg^{-1}$ soil, while for that of forest roadside soil it is 31.1 $mg \cdot kg^{-1}$ soil; in case of Cu, respective mean values for field roadside soil and forest roadside one are 32.3 and 12.0 $mg \cdot kg^{-1}$ soil, whereas for Mn the mean quantity in field roadside soil is 316.0 and in forest roadside one is 237.3 $mg \cdot kg^{-1}$ soil. Thus, the field roadside soil within the A and B roadside zones shows a higher level of accumulation of the analysed heavy metals in relation to that of forest roadside soil, ie by about a quarter times higher with respect to lead and manganese and by about two and a half times higher in the case of copper.

Table 2

Selected parameters and total content of Mn, Pb and Cu in top soil layer (0–0.1 m) from field and forest roadsides with degree of their contamination with Pb and Cu (according to Kabata-Pendias [15])

Study point/ roadside zone		Granulometric fraction ∅ < 0.02 mm [%]	pH_{KCl}	Mn	Pb	Cu	Pb	Cu
				$[mg \cdot kg^{-1}$ soil]			evaluation acc. to Kabata-Pendias [15]	
Field roadsides								
P1	A	8	7.51	352.8	32.1	21.1	I	I
	B	8	7.26	301.3	26.3	18.6	I	I
	C	11	6.95	238.4	19.0	9.8	0	0
	D	13	7.02	237.6	11.5	7.5	0	0
P2	A	10	7.15	367.9	96.6	101.4	I	III
	B	11	7.23	267.2	34.9	41.4	0	I
	C	13	6.93	342.7	5.6	6.6	0	0
	D	14	6.70	216.2	8.0	12.7	0	0
P3	A	9	7.13	400.7	44.0	29.8	I	I
	B	7	7.09	342.6	29.2	11.0	I	I
	C	8	6.80	304.0	13.9	4.9	0	0
	D	7	6.24	262.2	10.5	4.4	0	0
P4	A	8	7.26	405.5	44.1	24.5	I	I
	B	13	6.98	338.7	24.0	10.6	I	I
	C	16	6.72	340.7	12.7	7.8	0	0
	D	14	6.38	255.1	9.6	7.0	0	0
Forest roadsides								
L1	A	6	7.15	336.4	31.0	13.3	I	I
	B	5	6.80	208.7	21.3	7.6	I	0
	C	7	6.12	183.0	20.3	6.0	I	0
	D	4	5.45	111.5	15.6	2.7	0	0
L2	A	3	7.06	274.4	23.0	14.6	I	I
	B	6	6.89	286.4	36.2	19.6	I	I
	C	7	6.11	181.2	17.9	4.0	0	0
	D	6	5.89	172.1	15.8	3.5	0	0
L3	A	5	7.00	299.7	37.0	17.5	I	I
	B	3	6.67	245.0	39.2	8.2	I	0
	C	2	4.98	124.8	18.4	2.7	0	0
	D	4	4.67	132.7	11.0	1.7	0	0
L4	A	5	6.80	212.5	42.5	13.3	I	I
	B	3	5.56	62.5	18.0	1.8	0	0
	C	2	4.87	74.7	12.7	1.8	0	0
	D	3	4.70	46.0	12.6	2.1	0	0

P1– P4 permanent study points along field roads; L1–L4 permanent study points along forest roads; A – road shoulder edge; B – proper road shoulder; C – ditch; C – slope; 0 – natural content; I – increased content; III – medium-contaminated soil.

When assuming that the traffic volume on the compared road types is similar, the differences in the content of heavy metals in the roadside soil have to be a result of their different size composition and reaction.

Loose roadside vegetation cover on forest roadsides favours deposition of traffic pollutants directly on the soil surface. However, due to very acidic reaction and larger permeability (when compared with the soil from field roadsides), heavy metal chemical elements migrate faster in the soil profile and are only partly assimilable by plants [16, 17].

Compact roadside vegetation cover on field roadsides partly stops deposition of motor vehicle exhausts and dusts on plants and decreases their deposition on the

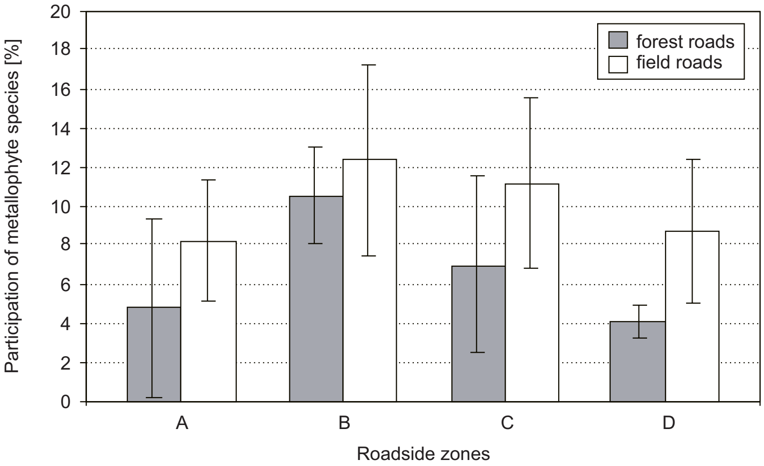

Fig. 1. Participation of metallophyte species in total number of species observed in following zones of forest and field roadsides: A – road shoulder edge; B – proper road shoulder; C – ditch; D – slope

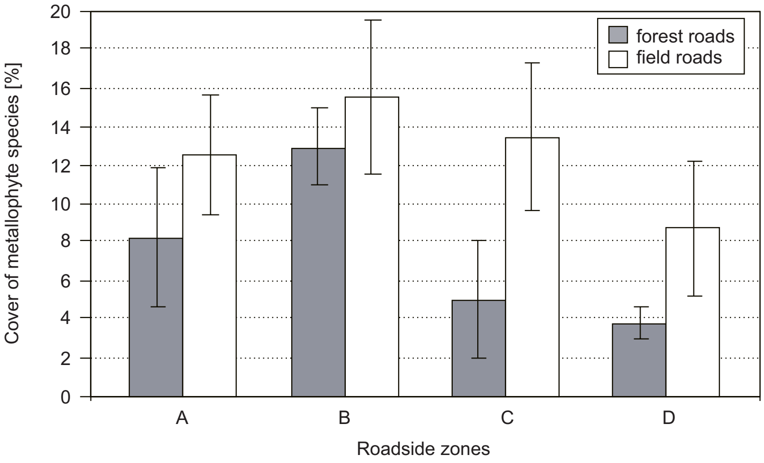

Fig. 2. Participation of metallophyte species in vegetation cover observed in following zones of forest and field roadsides: A – road shoulder edge; B – proper road shoulder; C – ditch; D – slope

roadside soil. However, a definitely neutral reaction and smaller permeability of soil from field roadsides affects the retention of examined heavy metal chemical elements in the top layer of soil [14]. The result of this is both a larger number of the metallophyte species found and their larger participation in vegetation cover on field roadsides (Fig. 1, Fig. 2).

Conclusions

1. The content of heavy metals in the forest anf field roadside soil is a result of their different granular composition and reaction.
2. Both the forest and field roadside soil pollution with examined heavy metals was increased in road shoulder edge and proper road shoulder zones. In following roadside zones (ditch and slope) the content of Mn, Pb and Cu was found at natural level.
3. The largest number of metallophyte species was observed in road shoulder edge and proper road shoulder zones both forest and field roads. In case of field roadsides found metallophyte species had larger participation in vegetation cover of these zones.

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ZAWARTOŚĆ METALI CIĘŻKICH W GLEBACH PRZYDROŻNYCH A PRZESTRZENNE ROZMIESZCZENIE GATUNKÓW METALOFITÓW NA POBOCZACH DRÓG NIZINY SZCZECIŃSKIEJ

Katedra Botaniki i Ochrony Przyrody, Zachodniopomorski Uniwersytet Technologiczny

Abstrakt: Przedstawiono wyniki badań dotyczące zawartości wybranych metali ciężkich w glebach poboczy dróg i przestrzennego rozmieszczenia metalofitów – gatunków roślin tolerujących obecność tych pierwiastków w glebie. Badaniami objęto strefy pobocza o łącznej szerokości 8 m, wzdłuż dróg o nawierzchni utwardzonej przebiegających przez kompleksy leśne i tereny rolnicze na Nizinie Szczecińskiej. Ogólna zawartość Mn, Pb i Cu w próbkach przydrożnych gleb śródpolnych i śródleśnych zmniejszała się w kolejnych strefach pobocza, przy czym gleby śródpolne w strefie 2 metrów od drogi kumulowały o 25 % więcej Pb i Mn oraz o ok. 60 % więcej Cu. Różnice w zawartości badanych metali ciężkich w próbkach wynikały z położenia strefy względem drogi oraz zróżnicowanego uziarnienia i odczynu gleb przydrożnych. Potwierdziła to analiza przestrzennego i ilościowego rozmieszczenia gatunków metalofitów na tle strefowej budowy poboczy dróg na badanym terenie.

Słowa kluczowe: flora przydrożna, metalofity, metale ciężkie, gleby zanieczyszczone

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Jarosław ZAWADZKI[1] and Piotr FABIJAŃCZYK[1]

REDUCTION OF SOIL CONTAMINATION UNCERTAINTY ASSESSMENT USING MAGNETIC SUSCEPTIBILITY MEASUREMENTS AND Co_Est METHOD

REDUKCJA NIEPEWNOŚCI OCENY ZANIECZYSZCZENIA GLEB PRZY WYKORZYSTANIU POMIARÓW PODATNOŚCI MAGNETYCZNEJ I METODY Co_Est

Abstract: The deposition of anthropogenic dusts originating mostly from industrial processes and solid fuel combustion causes the substantial changes in magnetic susceptibility of topsoil layers. Consequently, the magnetic susceptibility is one of the soil properties, which makes it possible to assess the soil contamination with heavy metals. Moreover, *in situ* field measurements of magnetic susceptibility are significantly less expensive and time-consuming than laboratory chemical analyses. However, the geochemical measurements are usually sparse and precise, whereas the magnetometric ones are numerous or even excessive, but not very exact. For these reasons, in order to assess the extent of soil contamination it should be performed both geochemical and magnetometric measurements at the same time, and then integrate them using some geostatistical methods such as cokriging. Because of usually too small set of geochemical measurements, this integration may be highly difficult task. In most cases, the modeling of auto-semivariance of primary variable and especially cross-semivariance in ordinary cokriging procedure become almost impossible.

This study presents the Co_Est procedure potential to reduce soil contamination uncertainty when geochemical measurements are too sparse, and magnetic susceptibility measurements serve as secondary data. For this purpose, topsoil pollution at few different size areas placed in forests or parks, located within the Upper Silesian Industrial Area was measured and analyzed. Then the maps of contaminations obtained using kriging and Co_Est methods were compared. In particular, reduction of uncertainty in soil contamination was quantified and discussed.

Key words: field magnetometry, topsoil magnetic susceptibility, heavy metals, geostatistics, data integration, Co_Est method, risk analysis

Magnetic susceptibility is one of the soil properties, which enables to assess the extent of soil contamination with heavy metals. The development of field magnetometry resulted from a need for fast and cheap methods for the detection of industrial pollution of soil. Recently, these measurements became recognized as a useful and effective

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[1] Environmental Engineering Systems Institute, Warsaw University of Technology, ul. Nowowiejska 20, 00–661 Warszawa, email: jarek97@yahoo.com, piotr.fabijanczyk@is.pw.edu.pl

method for detecting the potential soil pollution with heavy metals. Dust deposition of anthropogenic origin at the soil surface, which is a source of many magnetic particles, and amongst them heavy metals that cause also the increase of magnetic susceptibility of top soil layers. An increasing number of studies were carried out using magnetometry to assess the soil contamination with heavy metals [1–6]. Significant positive correlations were found between the magnetic susceptibility and the content of heavy metals of anthropogenic origin in soil [7, 8]. Due to these correlations, it is possible to estimate the extent of areas with heightened values of soil magnetic susceptibility, and simultaneously potentially polluted with magnetic compounds and accompanying heavy metals. Consequently, fast and cheap field magnetometric measurements can supplement or, in some specific situations, completely replace the chemical analyses.

Accordingly, field magnetometry offers a few types of measurement [9]. Most common types are surface measurements of soil magnetic susceptibility and measurements in the soil profile. In order to improve the precision of analyses, it may be advantageous to use simultaneously different types of soil magnetic susceptibility measurements and chemical ones. This can be done using some geostatistical methods, which enable to integrate information from different types of measurements.

This study presents the potential of Co_Est procedure to reduce soil contamination uncertainty when geochemical measurements are too sparse, and magnetic susceptibility measurements serve as secondary data. For this purpose, the topsoil pollution was measured and analyzed at few different areas placed in forests or parks within the Upper Silesian Industrial Area. Then the contamination maps obtained with kriging and Co_Est methods were compared. In particular, reduction of uncertainty in soil contamination was quantified and discussed.

Geostatistical methods

Geostatistics offers several tools for the data integration. Theses methods are useful when apart from measurements of primary variable, which are difficult to perform, expensive, time-consuming or too rarely sampled, also some additional measurements are available. Additional data are usually cheaper, less time-consuming, but also less precise in comparison with primary variable. Geostatistical data integration [10–12] enables to use both types of measurements and obtain spatial distributions more precise in comparison with the ones obtained with the use of only one type of measurement. One of the most common data integration methods is cokriging. Cokriging is a variety of kriging, which allows using multiple variables, correlated with each other. However, in some cases the application of cokriging can be difficult, especially in cases when only small data set of primary variable is available or samples are placed in very irregular way. In such situation, it is necessary to use different method of data integration. One of these methods is Co_Est [12].

The Co_Est method consists in the transformation of the secondary dataset into the primary one using the so-called pedotransfer functions (PF). PF's are regression equations or model, which relate the hard-to-measure field samples $Z(x_j)$ to $k = 1, 2, ..., t$ more basic and easy-to-measure properties $W(x_i)$.

$$Z(x_j) = \beta_0 + \sum_{k=1}^{t} \beta_k W(x_i) + \varepsilon_j$$

$Z(x_j)$ – values of the hard-to-measure filed samples – main variable;
$W(x_i)$ – values of the more basic and easy-to-measure properties – additional variables;
β_0, β_k – constants;
ε_j – random variable with mean equal zero and variance equal σ.

This transformation results in a larger data set of primary variable, which can be subsequently used in different geostatistical procedures like ordinary kriging. The Co_Est method also permits to estimate measurements errors both in primary and secondary data. In kriging method, the value estimated at unknown location, is calculated using linear combination of both variables:

$$Z^*(\mathbf{x}_0) = \sum_{k=j}^{N_1} a_j\, z(\mathbf{x}_j)$$

where $Z^*(\mathbf{x}_0)$ is the prediction at location $\mathbf{x}_{0,}$ $z(\mathbf{x}_j)$ is the j^{th} nearby sample primary value weighted by a_j, N_1 is the number of nearby samples of primary values.

Exemplary application in field magnetometry

The study area was located within Upper Silesian Industrial Area region, in the Repecki Park, located near Tarnowskie Gory town. The study area had irregular shape

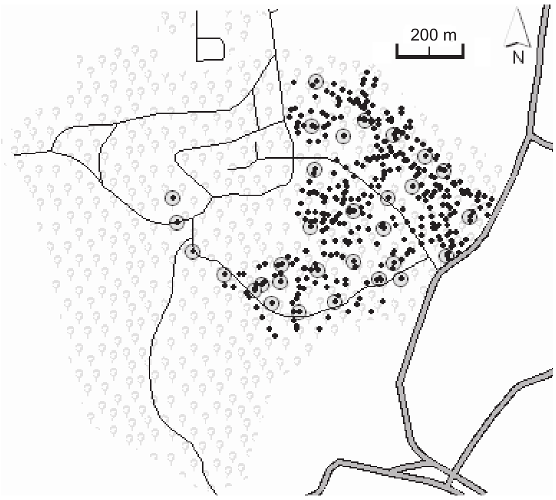

Fig. 1. The location of the study area and sample location of surface (denoted by black dot) and vertical measurements (denoted by gray dot)

with dimensions of about 1 km and 800 m. The park is placed near to the local public road but the area of the park is closed for traffic, and only available only for pedestrians.

At study area, different types of trees were present, both coniferous and deciduous ones. Some small areas were overgrown with brushwood. At entire study area, no water bodies or rivers were present.

The area was sampled with two types of measurements. The first one was the surface measurement of soil magnetic susceptibility carried out with MS2D Bartington sensor. The second one was the measurement of soil magnetic susceptibility in soil profile, carried out with SM400 sensor. The penetration range of MS2D sensor is about 10 cm, and for that reason, this measurement gives as a result an averaged soil magnetic susceptibility from depth from 0 to 10 cm [2–9]. The measurement in soil profile gives as a result a plot of magnetic susceptibility against the depth. In comparison with surface measurements, it is more precise, but it is also more time-consuming one. Results of these two types of measurements can be analyzed using geostatistical data integration in order to improve the precision of analyses.

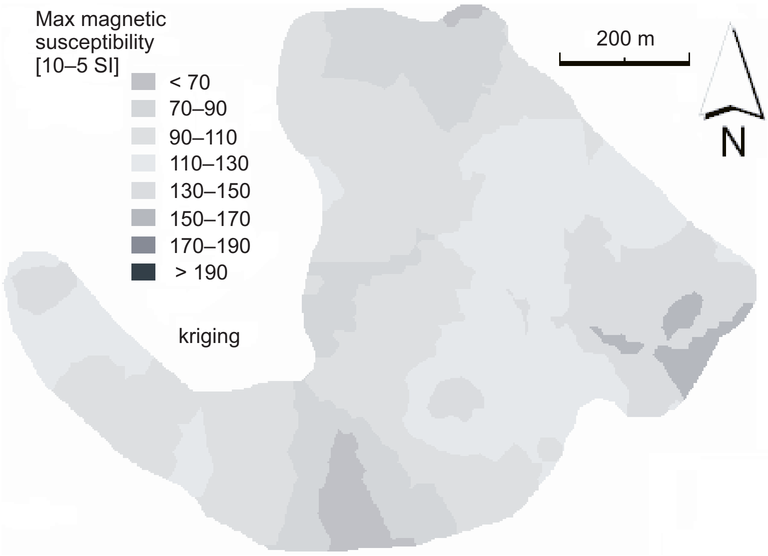

Fig. 2. Distribution of magnetic susceptibility in soil profile

The magnetic susceptibility usually shows characteristic distribution in the soil profile, and frequently maximum value of magnetic susceptibility is observed at the depth of several centimetre. This depth is directly connected with the thickness of the soil organic horizon. From each plot of the magnetic susceptibility in soil profile, the maximum value was picked up and used in further analysis as a main variable. Surface measurements of soil magnetic susceptibility were used as an additional one. In case of measured data set, the significant correlation exists between surface and vertical measurements, and the Pearson correlation coefficient was equaled about 0.64.

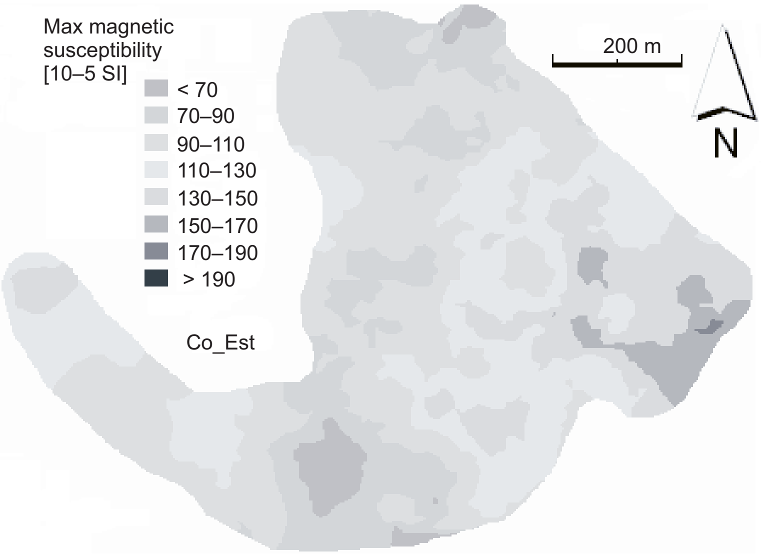

Fig. 3. Distribution of magnetic susceptibility in soil profile

In addition to the spatial distribution obtained with Co_Est method, kriging method was used, in order to compare precision of both methods.

Table 1

Prediction errors for spatial distributions calculated with Co_Est and kriging method

	Prediction error			
	Mean	Root mean square std.	Mean	Root mean square std.
	Area 1		Area 2	
Kriging	1.034	0.977	0.039	1.224
Co_Est	0.024	0.993	0.031	1.265

Conclusions

The results show that, it is possible to integrate different types of magnetometric measurements using Co_Est method. In case of the measurements of magnetic susceptibility at soil surface and in the soil profile, it is possible to obtain more precise spatial distributions in comparison with kriging method.

In case of chemical measurements data integration Co_Est method may also improve the precision of calculated spatial distributions. It is especially important in case of small and irregular datasets of chemical measurements.

Acknowledgements

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REDUKCJA NIEPEWNOŚCI OCENY ZANIECZYSZCZENIA GLEB PRZY WYKORZYSTANIU POMIARÓW PODATNOŚCI MAGNETYCZNEJ I METODY Co_Est

Wydział Inżynierii Środowiska, Politechnika Warszawska

Abstrakt: Depozycja pyłów pochodzenia antropogenicznego, pochodzących głównie ze źródeł przemysłowych i spalania paliw stałych, powoduje znaczne zmiany podatności magnetycznej górnych warstw gleby. Z tego względu podatność magnetyczna jest jedną z właściwości gleby, które mogą być wykorzystane w celu określenia stopnia zanieczyszczenia gleby metalami ciężkimi. Terenowe pomiary podatności magnetycznej są znacznie tańsze i mniej skomplikowane w porównaniu do analiz chemicznych. Ponadto pomiary chemiczne są zazwyczaj dokładniejsze i wykonywane z mniejszą gęstością powierzchniową niż pomiary magnetometryczne. Z powyższych powodów, celowe jest wykonywanie pomiarów obu rodzajów, a następnie zintegrowanie ich za pomocą metod geostatystycznych, takich jak np. cokriging. Jednak zazwyczaj ze względu na małą ilość danych chemicznych tego typu integracja jest bardzo trudna. Dokładne wymodelowanie wariogramów i wariogramów krzyżowych dla metody cokrigingu może być niemożliwe.

Niniejsza praca prezentuje możliwości zastosowania metody Co_Est w celu redukcji niepewności oceny zanieczyszczenia gleb, w przypadku gdy dostępna jest mała ilość pomiarów geochemicznych, a pomiary magnetometryczne służą jako dane uzupełniające. W tym celu wykonane zostały pomiary zanieczyszczenia gleb oraz pomiary magnetometryczne na kilku obszarach leśnych zlokalizowanych na terenie Górnośląskiego Okręgu Przemysłowego. Następnie wykonane i przeanalizowane zostały mapy rozkładów przestrzennych metodami krigingu i Co_Est.

Słowa kluczowe: magnetometria terenowa, podatność magnetyczna, metale ciężkie, geostatystyka, integracja danych, metoda Co_Est, analiza ryzyka

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Michał BODZEK[1], Aleksandra PŁATKOWSKA,
Mariola RAJCA and Karol KOMOSIŃSKI

FOULING OF MEMBRANES DURING ULTRAFILTRATION OF SURFACE WATER (NOM)

FOULING MEMBRAN PODCZAS ULTRAFILTRACJI WODY POWIERZCHNIOWEJ

Abstract: The results of studies focused on membrane fouling during surface water treatment by use of ultrafiltration, coagulation/sedimentation/ultrafiltration and in-line coagulation/ultrafiltration processes were presented. Medium- and low-molecular organic compounds (NOM) that are not rejecting in UF/MF process can be remove by use of pre-coagulation. The surface water used in the tests coming from Smieszek Lake located in Zory (Silesia province, Poland) contained organic matter of about 14 mg/dm^3 TOC. Aluminum sulfate was used in both coagulations (4.9 mg Al/dm^3, pH = 7.0). Molecular mass distribution in feed water and permeates was determined by use of high performance size exclusion (HPSEC). Applications of coagulation/sedimentation/ultrafiltration and in-line coagulation/ultrafiltration processes in water treatment allowed to get better quality of permeate than in ultrafiltration process alone. The smallest flux decline and the highest membrane capacity were observed in in-line coagulation/ultrafiltration process. Molecular weight distribution showed that integrated/hybrid processes allow rejecting molecules > 10 kDa in the highest degree. These molecules were responsible for membrane blocking as they deposit on surface and/or in membrane pores. The paper also presents impact hydrophobicity/hydrophilicity of NOM on UF membrane fouling. From isolated fractions the hydrophobic fraction of NOM caused the largest flux decline, while hydrophilic fraction – the smallest. Transphilic fraction pollutants were removed in highest grade. They might have a significant influence on membrane fouling.

Keywords: ultrafiltration, coagulation, natural organic matter (NOM), hydrophobicity/hydrophilicity, chromatography – HPSEC

Low-pressure membrane techniques are applied in drinking water production as an alternative for standard filtration. The conventional water treatment does not always guarantee total removal of low-molecular weight colloids and microorganisms. Ultrafiltration (UF) and microfiltration (MF) membranes separate colloids as well as ionic and nonionic organic substances depending on UF membrane limiting permeability (cut-off) and MF membrane pore sizes, however they pass through ionic inorganic

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[1] Institute of Water and Wastewater Engineering, Faculty of Energy and Environmental Engineering, Silesian University of Technology, ul. S. Konarskiego 18, 44–100 Gliwice, tel./fax: +48 32 237 2368, email: Michal.Bodzek@polsl.pl

substances. Especially they are able to retain protozoan, bacteria and viruses (membranes with cut-off < 100 kDa), natural high-molecular weight colored substances and other organic compounds (to a certain degree) as well as turbidity. Practically direct UF/MF processes are not able to retain medium and low-molecular weight compounds; however in hybrid configuration system (with coagulation or activated carbon) the removal of natural and synthetic organic matter is possible [1]. Difficulties in common application of UF/MF processes are connected with membrane lifetime. During the process, the accumulation of organic and/or inorganic matter on membrane surface or inside membrane pores takes place, what significantly decreases membrane yield. This phenomenon is generally known as fouling. Organic fouling connected with natural organic matter (NOM) is the most popular in water treatment processes [2]. NOM present in water comes mainly from soil and its amount and properties depend on climate, geology and topography of the source area and real changes, which take place during transport through lakes and rivers to the ocean [3]. NOM is a mixture of various organic compounds, both high-molecular weight (proteins, sugars, humus) and low-molecular weight like simple organic acids [4, 5]. It is possible to control fouling with use of special techniques, what allows elongating membrane lifetime and decreasing operational costs. These control techniques are physical methods, like periodic backwashing of membrane or membrane filtration process parameters optimization, and chemical methods (eg application of chemical cleaning agents). Proper membrane selection and membrane module construction are also significant regarding fouling [1]. Raw water pretreatment processes taking place before water introduction on membrane are very popular. Those pretreatment processes are: coagulation, adsorption on activated carbon, biological filtration and oxidation, and they are applied before proper UF/MF processes [6, 7]. Associated membrane systems are very useful especially in surface water treatment, as in comparison with groundwater surface water has high load of impurities.

Systems with coagulation allow improving the quality of treated water and decreasing membrane fouling caused by impurities present in raw water. Coagulation process can be run together with sedimentation or without it (in-line coagulation). Final effects of increase membrane yield when coagulation is applied mainly depend on character of impurities responsible for fouling and their interactions with membrane [1].

The aim of studies was to determine intensity of membrane fouling during treatment of water containing natural organic matter (NOM) in different configurations of the process: direct UF, integrated coagulation/sedimentation/ultrafiltration and hybrid in-line coagulation/ultrafiltration systems. The influence of coagulation on membrane filtration and membrane life-time as well as on fouling was analyzed. The molecular weight of NOM in dissolved fraction, supernatant after coagulation and in treated water (permeate obtained in integrated and hybrid process) was determined in order to find, which molecular sizes of compounds are responsible for fouling. The influence of hydrophilicity/hydrophobicity of organic matter (NOM) on UF membrane blocking also was investigated.

Experimental

The range of studies covered:

– surface water membrane filtration under constant pressure in direct ultrafiltration (membrane cut-off 30 kDa) and systems with standard and in-line coagulation;

– determination of molecular weght distribution in dissolved fraction, supernatant after coagulation and in permeate obtained in coagulation/sedimentation/ultrafiltration and in-line coagulation/ultrafiltration processes using size exclusion liquid chromatography (SEC);

– separation of dissolved fraction (< 0.22 μm) from surface water;

– fractionation of dissolved substances into hydrophobic (HPO), hydrophilic (HPI) and transphilic (TPI) fractions;

– membrane filtration of particular streams (dissolved substances, HPO, HPI and TPI) through cellulose ultrafiltration membranes.

Surface water from Smieszek lake (Silesia Region, Zory, Poland) contained organic substances in the amount of around 14 mgTOC/dm^3, was used in the studies.

Investigations were made with use of Stirred Ultrafiltration Cell Milipore CDS-10 System, model 8400. Figure 1 represents the scheme of the installation.

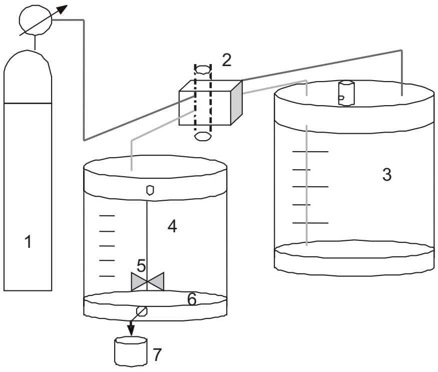

Fig. 1. Diagram of Milipore CDS-10 System installation: 1 – pressure source; 2 – selective valve; 3 – feeding tank; 4 – ultrafiltration cell; 5 – mixer; 6 – membrane; 7 – permeate

Continuous membrane filtration of feed of volume three times greater that the ultrafiltration membrane cell capacity was allowed by the system as it was equipped with selective valve CDS-10, which connected three main elements of installation: gas tank, ultrafiltration cell (capacity 400 cm^3) and feed tank (volume 800 cm^3). CDS-10 device cooperated with flat-sheet membranes in dead-end mode, in which feed was introduced perpendicularly to membrane surface.

Three types of membranes were used during studies: microfiltration membrane of pore diameter 0.22 μm in order to remove colloids (0.22 μm) from surface water, and two ultrafiltration membranes with cut-off 10 and 30 kDa. Both types of ultrafiltration membranes were used to determine the influence of hydrophilicity/hydrophobicity of NOM on membrane fouling. In proper investigations of water ultrafiltration in direct

UF, hybrid (in-line coagulation/ultrafiltration) and integrated (coagulation/sedimentation/ultrafiltration) processes membrane with cut-off 30 kDa was used. Table 1 represents characteristics of particular membrane given by producer.

Table 1

Characteristics of membrane used

Membrane type	MF membrane	UF membrane	UF membrane
Name of the product	Membrane filter Milipore Express Plus	UF membrane from Nadir	UF membrane from Millipore
Configuration	Flat-sheet		
Material	polyethersulphone	cellulose	regenerated cellulose
Pore diameter	0.22 μm	30 kDa	10 kDa
Area	38.5 cm^2		
Wettability	hydrophilic		
Pressure	0.1 MPa		

Surface water containing NOM was treated in direct UF, in hybrid system: in-line coagulation/UF and in integrated system: coagulation/sedimentation/UF. Ultrafiltration membrane with cut-off 30 kDa was used for that purpose. In coagulation process aluminum sulfate was applied. Coagulation process conditions: pH = 7.0 and coagulant dose D = 4.9 mgAl/dm^3 were determined by means of jar test. In coagulation/sedimentation process after coagulant addition rapid 1-minute-long and slow 30-minute-long mixing were applied. Then created flocs settled down for 30 minutes. Obtained supernatant served as feed in ultrafiltration process. In in-line coagulation (without sedimentation) coagulant was added directly to ultrafiltration cell and feed tank, and prepared feed was rapidly mixed for 1 minute and introduced to ultrafiltration process. Proper filtration tests were carried out under constant transmembrane pressure 0.1 MPa. During one-hour tests dependence of permeate flux (J_t) on time was determined, firstly after every minute, and after five minutes of run in five-minute periods. Obtained results were used in estimation of relative membrane permeability – $\alpha = J_t/J_0$, and allowed to determine tendency of fouling caused by particular NOM fractions. Simultaneously investigations focused on membrane effectiveness were carried out, during which retention coefficient (R) regarding TOC/DOC (total/dissolved organic carbon), absorbance UV_{254}, turbidity, pH, conductivity and aluminum content were determined.

Molecular weight distribution in streams created during treatment process was determined using high performance size exclusion chromatography (HPSEC). PL-GPC 50 Integrated GPC system chromatograph (Varian company), equipped with PL aquagel-OH 80 8 μm and PL aquagel 30 8 μm (300×7.5 mm) columns and UV detector, was used during studies. Phosphoric buffer of pH = 6.8 with 0.1 M HCl was applied as eluent. The column was calibrated using sodium polystyrenesulfonate. Detection was carried out at λ = 254 nm wavelength.

Fractionation of NOM using Amberlite XAD-7HP and XAD-4 resins (Rohm&Haas Company) was made in order to determine influence of hydrophilicity/hydrophobicity on membrane fouling. Fractionation procedure, described in detail in [8], allowed to obtained hydrophobic (HPO), intermediate (transphilic – TPI) and hydrophilic (HPI) fractions. Fractionation was made with water from which 0.22 μm diameter particles were already removed and which was acidified to pH = 2 using 0.1 M HCl. Particular fractions were introduced to ultrafiltration process carried out under constant trans-membrane pressure 0.1 MPa and dependence of permeate flux (J_t) on time and membrane relative permeability ($\alpha = J_t/J_0$) were estimated regarding DOC and UV_{254} absorbance.

Every proper UF required application of new membrane, which firstly was conditioned by five-hour filtration with deionized water. The operation was run under pressure 0.1 MPa, and was necessary to remove protection layer from the membrane and condition it. During deionized water filtration volumetric water stream (J_0) was determined.

Results and discussion

Fouling during water treatment in direct UF and coagulation/UF systems

Relative permeability changes (for transmembrane pressure 0.1 MPa) during direct UF, integrated (coagulation/sedimentation/UF) and hybrid (in-line coagulation/UF) process run are shown in Fig. 2.

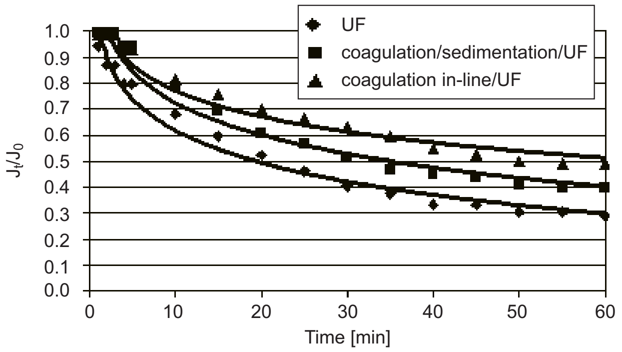

Fig. 2. Membrane relative permeability change during filtration for all water purification processes

Application of coagulation/sedimentation/UF and in-line coagulation/UF systems allows obtaining higher organic compounds retention coefficients in comparison with direct UF process (Table 2).

In integrated/hybrid processes TOC retention was more than 40 %, DOC was around 30 % and UV_{254} achieved more than 50 %, while for the direct process those values were less than 30 % for TOC, DOC around 10 % and UV_{254} around 40 %. In all cases turbidity was removed in more than 98 %. In integrated/hybrid processes organic compounds removal degree (which did not achieved even 50 %) is connected with SUVA (specific ultraviolet absorption SUVA = UV_{254}/DOC) value of raw water (2.62 $dm^3/mg \cdot m \leq 3$ $dm^3/mg \cdot m$), which does not indicate the susceptibility of water to DOC removal in coagulation process. According to that 8.8 % of TOC was removed.

Table 2

Physicochemical parameters of raw and purified water and retention coefficients of pollutants obtained during water purification processes

Process		TOC [mgC/dm^3]	DOC [mgC/dm^3]	UV_{254} [1/cm]	Turbidity [NTU]	pH	Conductivity [mS/cm]
Ultrafiltration alone UF	Raw water	11.92	9.34	0.222	10.03	8.00	0.446
	Permeate	8.43	8.43	0.134	0.12	7.98	0.432
	Retention R [%]	29.3	9.70	39.6	98.80	—	—
Coagulation /sedimentation	Raw water	11.27	—	0.217	16.63	7.00	0.428
	Supernatant	10.28	—	0.155	5.93	6.68	0.457
	Retention R [%]	8.8	—	28.6	64.3	—	—
Coagulation /sedimentation/UF	Raw water	11.27	9.34	0.217	16.63	7.00	0.428
	Permeate	6.60	6.60	0.092	0.20	6.92	0.481
	Retention R [%]	41.4	29.30	57.6	98.8	—	—
Coagulation in-line/UF	Raw water	11.15	9.34	0.208	16.28	7.00	0.457
	Permeate	6.28	6.28	0.090	0.34	6.93	0.471
	Retention R [%]	43.7	32.80	56.7	98.10	—	—

Volumetric permeate flux in integrated/hybrid systems was higher than one obtained in direct UF. Application of in-line coagulation before membrane filtration improves membrane yield in 18 % comparing with standard coagulation. The effect of membrane fouling was determined using relative permeability α. After one-hour filtration α coefficient decreased in direct UF to 0.29, in integrated process to 0.40 (coagulation/sedimentation/UF), and in hybrid process to 0.49 (in-line coagulation/UF). This proves that application of in-line coagulation before UF process mostly decreases membrane fouling.

Pre-coagulation applied before membrane filtration results in creation of particles with greater diameters, which accumulate on membrane surface blocking membrane pores in lower degree. It is confirmed by chromatographic analysis (Fig. 3, Tables 3 and 4). Dissolved fraction contained 38.7 % of particles in range > 10 kDa, while in supernatant 39.5 % of particles varied from 1–5 kDa. Dissolved fraction was more diversified regarding particles sizes than supernatant, what was confirmed by poly-dispersion of samples (d = 5.71 and d = 4.15). Investigations showed that standard coagulation caused greater fouling compared with in-line coagulation. Filtration cake created during in-line coagulation, as distinguished from standard coagulation and direct UF, probably possessed greater porosity and lower ability to bond with membrane surface, what limited membrane contamination, especially inside its pores [9].

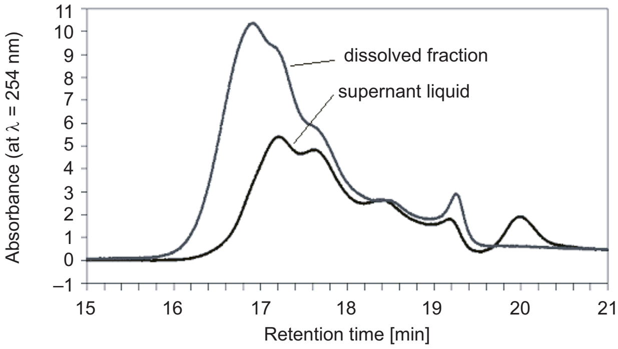

Fig. 3. Chromatograms of NOM in dissolved fraction and water after coagulation/sedimentation

Table 3

Distribution of NOM molecular weight in water after sedimentation and in permeates after coagulation/sedimentation/UF and coagulation in-line/UF processes

Apparent molecular weight [Da]	Percent of fraction [%]			
	Dissolved fraction	Supernatant	Permeate in-line	Permeate on-line
> 10000	38.70	13.69	8.87	8.92
10000–5000	22.99	24.15	24.31	23.96
5000–1000	25.20	39.46	42.68	42.14
< 1000	13.12	22.70	24.14	24.98

Table 4

Comparison of molecular weight data for dissolved fraction, water after sedimentation and permeates after coagulation/sedimentation/UF and coagulation in-line/UF processes

Characteristic data	Dissolved fraction	Supernatant	Permeate in-line	Permeate on-line
Mp [Da]	12654	7334	6936	7154
Mn [Da]	1679	1172	1141	1093
Mw [Da]	9589	4863	4140	4117
Mz [Da]	17486	9338	7454	7513
d [-]	5.71	4.15	3.63	3.77

More detailed analysis of molecular weight distribution of fractions obtained during water treatment can be made basing on chromatographic data collected in Tables 4 and 5 and in Figures 4 and 5. Data described below is shown in Table 4:

– M_n – average molar number, $M_n = (\Sigma\ N_iM_i)/(\Sigma\ N_i)$,
– M_w – average molecular weight, $M_w = (\Sigma\ N_iM_i^2)/(N_iM_i)$,
– M_z – the value calculated from the equation, $M_z = (\Sigma\ N_iM_i^3)/(N_iM_i^2)$,
– M_p – molecular weight estimated for maximum peak,
– d – polydispersion, $d = M_w / M_n$ (d = 1 for polymer of defined molecular weight).

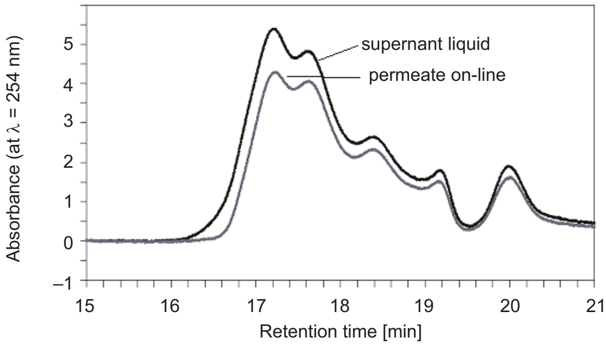

Fig. 4. Chromatograms of NOM in water after coagulation/sedimentation and permeate after coagulation/sedimentation/UF process

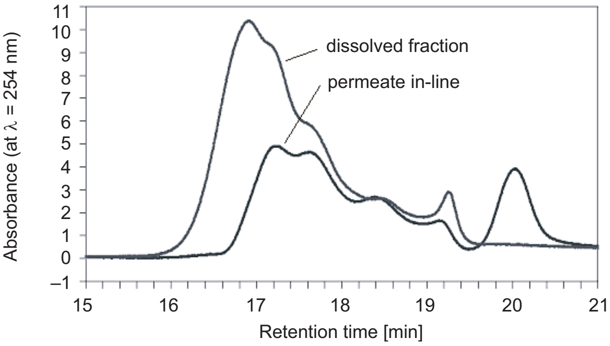

Fig. 5. Chromatograms of NOM in dissolved fraction and permeate after coagulation in-line/UF

Comparing molecular weight distribution of on-line (coagulation/sedimentation/UF) and in-line (in-line coagulation/UF) permeates with dissolved fraction in can be noticed that both permeates are characterized with the same curve progress. Both permeates have similar polydispersion (d = 3.63 and d = 3.77, respectively), lower than polydispersion of supernatant. It can be concluded that hybrid and integrated process separate particles with the same molecular weight. Analysis of particle size distribution showed, that in dissolved fraction particles > 10 kDa predominated, while in other cases more particles were in range 1–5 kDa.

Dissolved fraction comprised of particles > 10 kDa in 38.7 %, 23 % were particles in the range of 5–10 kDa, 25.2 % in the range of 1–15 kDa, and 13.1 % of particles smaller than 1 kDa. Application of coagulation and sedimentation changed particles size distribution. The greatest particles (> 10 kDa) were retained in 65 %. On the other hand, coagulation turned out to be ineffective process, as it allowed removing only around 9 % of TOC. It can be explained by the fact that analyzed water has hydrophilic properties with greater amount of non-humic substances, which are still present in water after coagulation [10]. In supernatant increase of the amount of particles with size varying from 5–10 kDa was negligible comparing with dissolved fraction, the amount of particles of size 1–5 kDa increased 1.5 times and the amount of particles < 1 kDa was almost 2 times greater.

Molecular mass distributions in permeate after coagulation/sedimentation and in-line coagulation/sedimentation are very similar. It confirms the fact, that it is difficult to estimate which method should be applied in investigated process treatment. In both cases similar retention coefficients of particular impurities indicators were obtained. Particles > 10 kDa were separated (R = 35 %). The amount of particles of range 1–5 kDa increased around 17 %, comparing with dissolved fraction, while regarding supernatant this increase was negligible.

To sum up, particles greater than 10 kDa were separated in the highest degree in integrated/hybrid processes, what had an influence on UF membrane fouling. Particles from range 5–10 kDa were not separated. The amount of particles < 5 kDa actually increased. The most probable explanation of this phenomenon is connected with coagulation process, during which created flocs were not big enough to be effectively separated, and particles of sizes smaller than membrane pores passed through membrane.

Influence of hydrophilicity/hydrophobicity of NOM on UF membrane fouling

Organic substances fractionation

Fractionation with microfiltration membrane filtration (0.22 μm) and adsorption on Amberlite XAD7HP/4 resins allowed isolating 4 fractions from surface water:

- dissolved (< 0.22 μm),
- hydrophobic HPO,
- transphilic (TPI),
- hydrophilic (HPI).

Dissolved fraction was 65 % of total organic substances content in analyzed natural water. Table 5 presents mass balance of organic substances in water containing dissolved substances after acidification to pH = 2, and also in particular fractions. Mass balance analysis was carried out basing on DOC measurements.

Table 5

Mass balance of organic substances in surface water

Sample	DOC	Sample volume V	DOC mass [m]	Percent
	[mgC/dm^3]	[dm^3]	[mg]	[%]
Dissolved fraction – after acidification	8.38	5.0	41.90	100.00
Hydrophobic fraction	31.76	0.310	9.85	23.51
Transphilic fraction	17.65	0.322	5.68	13.56
Hydrophilic fraction	5.18	5.0	25.90	61.81
Σ (HPO + TPI + HPI)			41.43	98.88

In investigated water the greatest part of natural organic substances comprised hydrophilic fraction – around 62 % DOC. Hydrophobic fraction was around 24 % of DOC, while the smallest part was transphilic fraction containing around 14 % of DOC. However, mass balance of organic substances, measured as DOC of particular NOM fractions, is not equal to 100 %. In feed introduced to resins the amount of organic substances was 1.12 % higher than sum of isolated fractions. It is connected with presence of wall effect (0.1 M NaOH used in elution of absorbed particles probably did not have a good contact with bed, simply streamed down column walls and did not elute all absorbed particles) or with way of elution of absorbed particles, what is equivalent with resins regeneration. Elution was carried out in the direction of proper feed flow, what caused migration of washed particles from upper bed layer to lower parts and resulted in contamination of unused layers. Characteristic of particular fractions is shown in Table 6.

Table 6

Characteristics of NOM fractions isolated from surface water

Probe	DOC	UV_{254}	SUVA	Turbidity	pH	Conductivity
	[mgC/dm^3]	[1/cm]	[dm^3/mg · m]	[NTU]	[-]	[mS/cm]
Dissolved fraction	8.38	0.220	2.62	0.45	2.0	4.49
Hydrophobic fraction	31.76	0.917	2.89	1.79	2.0	8.90
Transphilic fraction	17.65	0.345	1.95	2.04	2.0	8.77
Hydrophilic fraction	5.18	0.058	1.12	0.35	2.0	5.57

Dissolved fraction contained all isolated NOM fractions like aromatic and aliphatic compounds and possessed lower SUVA value comparing with HPO, however regarding HPI and TPI this value was higher, what agrees with previously observed dependences [8]. Analysis of obtained results allows to conclude that organic substances present in natural water have combined character what is confirmed by SUVA = 2.62 dm^3/mg · m. Literature [11] suggests that in this range of ultraviolet absorbance (SUVA $\leq$ 3 dm^3/mg · m) the degree of DOC removal during coagulation does not exceed 30 %. In such a case sorption methods are recommended.

Ultrafiltration membrane fouling investigations

Filtration of dissolved, hydrophobic, transphilic and hydrophilic fractions was carried out using two types of cellulose membranes of cut-off 10 kDa (regenerated cellulose) and 30 kDa (cellulose). Particular streams were standardized regarding pH, conductivity, DOC and temperature before they were introduced to membrane filtration. Obtained results are presented graphically in Fig. 6 and 7.

During one-hour filtration continuous decrease of membrane yield was observed. This decrease was higher for 30 kDa cut-off membrane in comparison with 10 kDa cut-off membrane (Table 7).

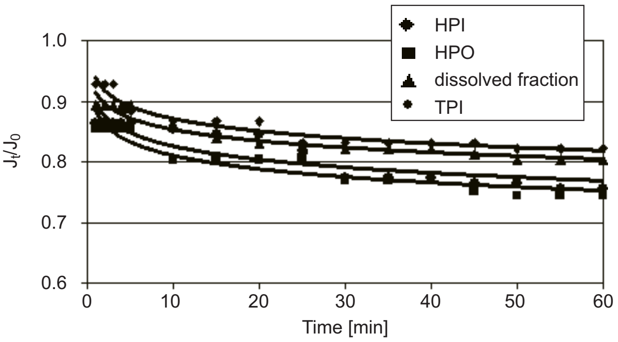

Fig. 6. Relative permeability change during filtration of dissolved, HPO, TPI and HPI fractions through membrane with cut-off 10 kDa

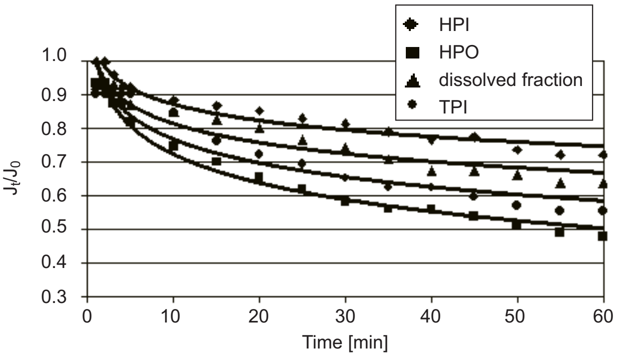

Fig. 7. Relative permeability change during filtration of dissolved, HPO, TPI and HPI fractions through membrane with cut-off 30 kDa

Table 7

Comparison of relative permeability decline for ultrafiltration membranes with cut-off 10 and 30 kDa

Probe	Membrane relative permeability decline [%]	
	10 kDa	30 kDa
Dissolved fraction	19.6	36.0
Hydrophobic fraction	25.6	52.1
Transphilic fraction	24.5	44.4
Hydrophilic fraction	17.8	27.8

In both cases fouling potential regarding permeate flux decrease appeared in the same order: hydrophobic fraction > transphilic fraction > dissolved fraction > hydrophilic fraction. The highest decrease of permeate flux was caused by hydrophobic fraction, which contained mainly high molecular weight DOC fraction. The greatest effectiveness of membranes separation was obtained during filtration of hydrophilic fraction, which was composed mainly from non-humic low-molecular weight substances [12]. Both membranes effectively separated transphilic fraction pollutants

(R = 79 %, R = 22.78 %). It can be said that DOC fractions successfully removed by membranes are not the same fraction, which causes higher decrease of flux. Similar results obtained by Zularisam et al [10], however in their studies on the one hand the highest flux decrease was obtained for HPI fraction, but on the other hand from this fraction the lowest amount of DOC was removed. The significant influence of hydrophobic fraction on fouling was already described in literature [13–16].

Membrane of cut-off 10 kDa separated in the lowest grade hydrophobic fraction impurities (R = 26.7 %), while membrane of cut-off 30 kDa was inefficient separating dissolved fraction (R = 4.83 %). It is undoubtedly connected with size of separated particles. Probably particles of size similar or smaller than membrane pore sizes pass through and are not separated by membrane.

Conclusions

Application of hybrid/integrated system in water containing organic matter treatment allowed to obtain permeate of better quality in comparison with direct UF, what is confirmed by higher organic compounds retention coefficients. In-line coagulation/UF process decreased UF membrane fouling most effectively and improved membrane yield. Coagulation/sedimentation/UF process turned out to be less effective, as it removed only around 9 % of TOC. It is connected with raw water value of SUVA = 2.62 $dm^3/mg \cdot m$. In that case sorption methods are recommended.

Molecular weight distribution in analyzed water showed that particles of size > 10 kDa were effectively separated in integrated/hybrid systems. Probably those particles are responsible for membrane blocking as they deposit on membrane surface and/or inside its pores.

Dissolved fraction accounts for 65 % of total organic matter content in analyzed natural water. From all isolated fractions, hydrophilic fraction had the greatest part and contained around 62 % of DOC. Hydrophobic NOM fraction caused greatest decrease of permeate flux, while hydrophilic fraction the lowest. It shows that HPO has the highest influence on membrane fouling caused by natural organic matter. Membrane of cut-off 10 kDa had higher efficiency in organic compounds removal in comparison with 30 kDa cut-off membrane. Both membranes separated mainly transphilic fraction impurities, which can significantly increase fouling. According to that it is claimed that DOC fractions removed most effectively by membrane are not the same fraction, which causes higher decrease of permeate flux.

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FOULING MEMBRAN PODCZAS ULTRAFILTRACJI WODY POWIERZCHNIOWEJ

Instytut Inżynierii Wody i Ścieków, Politechnika Śląska

Abstrakt: Przedstawiono wyniki badania intensywności foulingu membran podczas oczyszczania wody naturalnej w procesie jednostkowym ultrafiltracji, zintegrowanym koagulacji klasycznej/ultrafiltracji oraz hybrydowym koagulacji in-line/ultrafiltracji zawierającej naturalne substancje organiczne (NOM). Wstępna koagulacja umożliwia usunięcie średnio- i małomolekularnych związków organicznych, które w samodzielnym procesie UF/MF nie są usuwane. W badaniach stosowano wodę powierzchniową z jeziora Śmieszek, zlokalizowanego na terenie miasta Żory, charakteryzującą się zawartością związków organicznych na poziomie ok. 14 mg TOC/dm^3. W procesie koagulacji zastosowano siarczan glinu (4,9 mg Al/dm^3, pH = 7,0). W strumieniach powstających podczas procesu oczyszczania wyznaczono rozkład mas molekularnych za pomocą HPSEC. Zastosowanie układu hybrydowego/zintegrowanego do oczyszczania wody zawierającej substancje organiczne pozwoliło na uzyskanie permeatu lepszej jakości niż w bezpośredniej UF. Ponadto proces koagulacji in-line/UF w największym stopniu zmniejszył fouling membrany UF i w konsekwencji polepszył jej wydajność. Rozkład mas molekularnych wykazał, iż w procesach zintegrowanych/hybrydowych w największym stopniu zostały zatrzymane molekuły o rozmiarach > 10 kDa. Molekuły te są odpowiedzialne za zjawisko blokowania membran, osadzając się na powierzchni i/lub w porach. Określano również wpływ hydrofilowości/hydrofobowości substancji organicznej na zjawisko blokowania membran ultrafiltracyjnych. Spośród wyizolowanych frakcji NOM frakcja hydrofobowa NOM spowodowała największy spadek strumienia permeatu, podczas gdy hydrofilowa najmniejszy. W największym stopniu zatrzymane zostały zanieczyszczenia frakcji transfilowej, które mogą znacząco przyczynić się do zjawiska foulingu.

Słowa kluczowe: ultrafiltracja, koagulacja, naturalne substancje organiczne (NOM), hydrofilowość/hydrofobowość, wysokosprawna chromatografia wykluczenia objętościowego (HPSEC)

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Wiesław KOŹLAK[1]

APPLICATION OF SODIUM WATER GLASSES FOR THE REMOVAL OF NICKEL SALTS FROM WATER ECOSYSTEMS*

WYKORZYSTANIE SZKIEŁ WODNYCH SODOWYCH DO USUWANIA SOLI NIKLU Z EKOSYSTEMÓW WODNYCH

Abstract: The properties of nickel, particularly toxic properties of nickel compounds were presented. Using the turbidimetric method, the systems containing sodium water glasses of different moduli and selected nickel salts were studied. It was demonstrated that high turbidity values in the studied systems indicate the reaction of Ni^{2+} ions with silicate forms and that is why sodium water glasses can be used to remove Ni^{2+} ions from water ecosystems, for instance wastewaters.

Keywords: sodium water glasses, turbidimetry, nickel salts, water ecosystems

Among the vast number of chemical compounds, not all of them are worthy of mass production, mostly because of their limited application possibilities, while their cost of production or synthesis is high. Sodium water glasses (sodium silicates) belong to the group of chemical compounds, which find versatile applications, though the knowledge of their properties and structure and particularly of their aqueous solutions is only slight [1, 2]. Also, there is lack of unequivocal opinions of researchers regarding the mechanisms of water glasses interactions [3, 4].

The analysis of recent literature indicates wide spectrum of studies, although because of significant topical scatter, obtained results do not lead to the solution of problems pervading for years [5].

Sodium silicates have to be counted among mass products of chemical industry, which in Poland did not yet find adequate application. Foreign production of water glasses, which are a foundation of many branches of economy is much higher than that

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[1] Faculty of Civil Engineering, Mechanics and Petrochemistry, Warsaw University of Technology, Institute of Chemistry, ul. I. Łukasiewicza 17, 09–400 Płock, tel./fax. 24 262 36 91, email: ich@pw.plock.pl

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in Poland. Sodium silicate belongs to the group of mass products, having in Poland the fundamental base for their production: silicon dioxide (SiO_2) in the form of sand and sodium carbonate (Na_2CO_3). Consequently, in Poland there are adequate conditions for the production of sodium silicates [2].

In Poland the sole producer of sodium water glasses is the “Rudniki” S.A. Chemical Plant, near Częstochowa. Five types of water glasses are produced there, denominated as 150, 149, 145, 140 and 137.

An attempt to use sodium water glasses for the purification of wastewaters their reactions with selected ions of transition elements

Literature concerned with the evaluation of interactions of water glasses solutions with selected electrolytes is very modest. There are publications on the influence of calcium and magnesium salts, ions termining the hardness of water, on the behaviour of systems containing water glasses and iron(II and III) salts, because of the importance of silicates in the anti-corrosion protection of communal and industrial water grids [7–9]. In the previous studies in this area the following methods were applied: potentiometric with the use of ion-selective calcium electrode, viscosimetric, based on the viscosity measurements or the product of viscosity and density measurements for concentrated solutions, as well as turbidimetric method [3, 4].

The use of sodium silicates in the processes of water purification, particularly wastewaters, with variety of composition (including the content of inorganic salts) is sometimes hard to evaluate, it indicates the necessity to carry out studies on “water glasses – selected metal salts” systems.

It was mentioned that there are some results and attempts to evaluate the reactions of silicates with magnesium, calcium, iron(II and III) ions, however there is lack of studies regarding the reactions of water glasses with transition metal ions. Preliminary studies in this area indicate that the most useful method of studies is the turbidimetric method [6–8]. It is based on the formation of a soluble, colloidal silicate of a studied salt as a result of the reaction of soluble silicate forms with studied salts and the measurement of light intensity dispersed by the formed silicate. The ability to form the silicate of a studied salt and the nature of changes of the intensity of dispersed light depend on the chemical composition of the silicate solution and its silicate modulus (M_k).

Occurrence, properties, uses and toxicity of nickel

Nickel forms many individual minerals such as pentlandite $(Fe, Ni)_9S_8$, chloanthite $NiAs_2$, gersdorffite NiAsS [10]. Nickel is a silvery-white metal, in normal conditions does not react with air or water. It easily dissolves in diluted acids, producing Ni^{2+} ions and H_2. Concentrated HNO_3 and *aqua regia* cause passivation of nickel [11]. In many different compounds exists on the +2 level of oxidation, such as NiO, $Ni(OH)_2$, NiS, $NiCl_2$, $NiSO_4 \cdot 7H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$, $NiCO_3 \cdot 6H_2O$ [10,12]. Nickel is predominately used as an additive for steel. Both pure nickel and its alloy with copper is used *eg* to make coins and everyday-use items, heating systems, rheostats and anti-corrosion layers. Nickel exhibits strong catalytic properties in the reactions of hydrogenation of organic compounds (the so-called Raney nickel) [10].

Nickel is not essential for the adequate functioning of most living organisms, however it was found that some plants cannot normally grow in the absence of it in soil. Mobility of nickel in the soil environment is strongly influenced by the granulometric and mineralogical composition of soils. Its occurrence in soil depends on the concentration of nickel in rocks. During the process of erosion, nickel is released forming mobile ionic form and is absorbed by iron and manganese hydroxides. Nickel is easily uptaken by plants, if it is present in soil in its mobile forms. In plants nickel is very mobile and is easily transferred to the upper parts of the plant. Vegetables accumulate more nickel than fruits. Excess of nickel causes the damage of assimilation apparatus – particularly in vegetables. The most frequent symptom of nickel excess is an illness caused by elimination of iron from physiological functions. Roots are also damaged, which become thicker, tawnier and do not grow normally. Moreover, this metal causes disruption of anion-cation equilibrium in green parts of the plants, which perturbs the metabolism of calcium and iron. Nickel uptaken by human organisms from food is in most part excreted, on the other hand nickel inhaled with atmospheric dust accumulates in lungs and causes damage to the mucous membranes. Lack of nickel causes the inhibition of growth and reduction of hemoglobin level in blood as well as epidermis changes and disruption of pigmentation [13]. Nickel is a microelement necessary for the proper functioning of an organism, is an activator of some enzymes and influences the hormonal activity. Nickel was thought to be a toxic, carcinogenic metal, however in 1970 it was demonstrated that is a microelement necessary for the proper functioning of an organism. In plant tissues nickel normally occurs in concentrations up to 3 ppm, while in animal tissues from 0.1 to 9 ppm. Nickel enters human organisms through alimentary and breathing systems [14]. Deficit of nickel causes degradation of liver, changes in pigmentation, deformation of bones, swelling of joints, reduction of oxygen absorption and increase of fatty tissues. Excess of nickel causes changes in the structure of nucleic acids leading to oral cavity, throat and lung cancer, as well as the so-called nickel eczema. It accumulates in lymphatic nodes, river phytoplankton and bottom residues and in tobacco leaves. One cigarette contains from 1.6 to 3.1 μg of nickel [15]. Concentration of nickel increases in the blood serum after an infarct and as a result of shocks and burns. Also in cancer tissue the concentration of nickel is elevated [14,15]. It was demonstrated that there is a correlation between the occurrence of oral cavity and intestine cancers and the concentration of nickel in potable water. That is why the emission of nickel to the environment as a result of combustion of fuels (particularly coal and oil), production of metallurgical and asbestos dusts, cigarette smoking, wastewater and sludge dumping from refineries, galvanizing plants and alkaline batteries production plants has to awake anxiety. This is the cause why there is a lot of nickel in soils and leafy plants.

Generally, nickel is not a component of natural waters. Its presence depends on the composition of soil. Nickel can occur in water in a dissolved form as a bivalent cation or complex ions – mostly cyanide complex, and in an undissolved form as a cyanide, sulphide, carbonate or hydroxide. The concentration of nickel in surface waters is regulated by law.

For the determination of nickel, a colorimetric method with dimethylglyoxime is used in the range of nickel concentration from 0.2 to 20 mg/dm^3 Ni. Samples have to be preserved by the addition of 2–5 cm^3 of concentrated nitric acid to 1 dm^3 of water. Cyanide containing samples may not be preserved. Nickel ions in slightly ammoniac solution, in the presence of strong oxidant (bromine) react with dimethylglyoxime, producing red-coloured complex compound. Intensity of coloration is proportional to the concentration of nickel. By the direct method nickel can be determined in concentrations from 0.2 to 5 mg/dm^3 Ni [16].

Experimental

Sodium water glasses produced by Swedish company Eka-Chemicals in Bohus Div PK Sektor SC were used in this study [17].

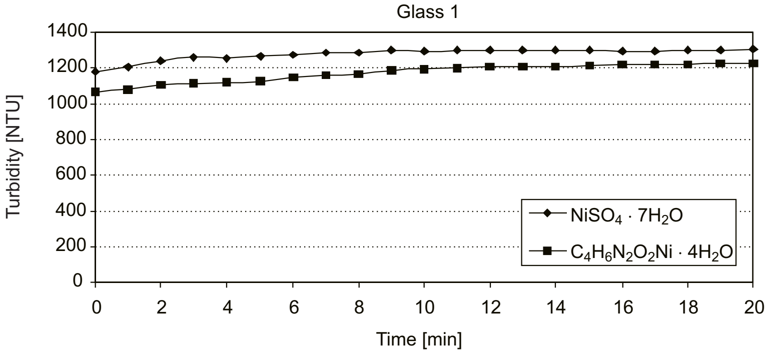

Fig. 1. Turbidity as function of time in the systems containing sodium water glass (M_k = 3.243) and studied salts

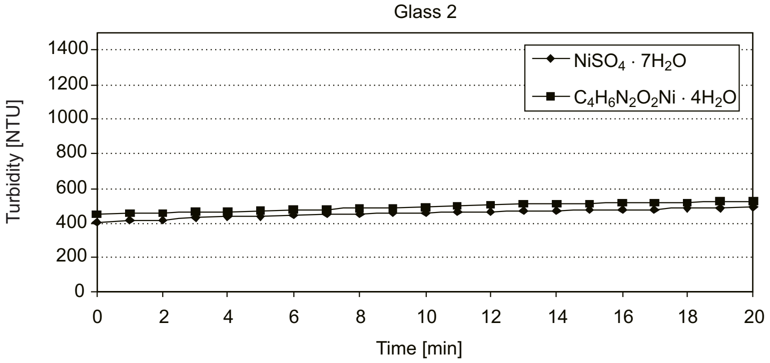

Fig. 2. Turbidity as function of time in the systems containing sodium water glass (M_k = 3.264) and studied salts

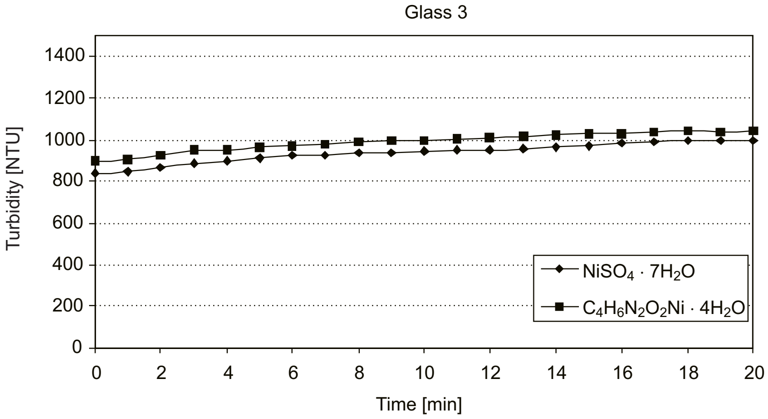

Fig. 3. Turbidity as function of time in the systems containing sodium water glass ($M_k = 3.289$) and studied salts

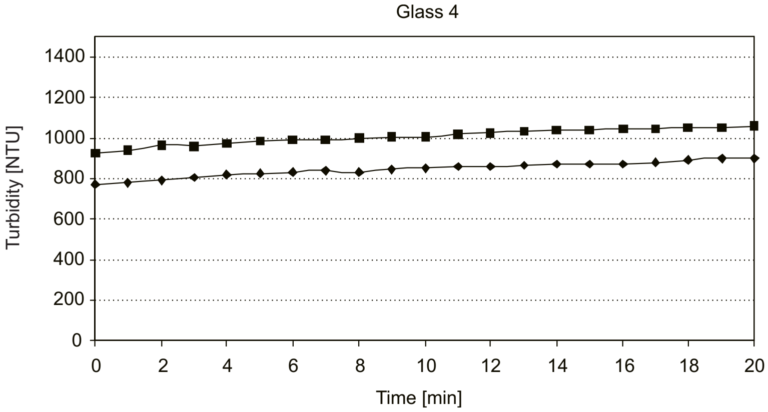

Fig. 4. Turbidity as function of time in the systems containing sodium water glass ($M_k = 3.412$) and studied salts

$NiSO_4 \cdot 7H_2O$ and $C_4H_6N_2O_2Ni \cdot 4H_2O$ were used as nickel salts. The concentration of nickel ions was 8 mmol/dm^3.

Experimental results in a form of turbidity curves are presented in Figures 1–4.

Conclusions

Addition of nickel salts to the water glass causes the precipitation of colloidal silicates, which are formed immediately, *ie* in the beginning phase of the measurement, without further significant increase of turbidity in time.

The type of silicate, *ie* its silicate modulus, molecular composition of its aqueous solutions and the type of used salt significantly influence the formation of colloidal silicates.

Taking into account the toxicity of nickel salts, sodium water glasses can be used to remove Ni^{2+} ions from aqueous media, such as wastewaters. High values of turbidity indicate significant reactivity of Ni^{2+} with silicate forms.

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WYKORZYSTANIE SZKIEŁ WODNYCH SODOWYCH DO USUWANIA SOLI NIKLU Z EKOSYSTEMÓW WODNYCH

Instytut Chemii, Wydział Budownictwa, Mechaniki i Petrochemii w Płocku,
Politechnika Warszawska

Abstrakt: Przedstawiono właściwości niklu ze szczególnym uwzględnieniem tosyczności jego związków. Metodą tubidymetryczną badano układy „różnomodułowe szkła wodne sodowe-wybrane sole niklu". Wykazano, że duże wartości zmętnień w badanych układach wskazują na reagowanie Ni^{2+} z formami krzemianowymi i dlatego szkła wodne sodowe można wykorzystać do usuwania jonów Ni^{2+} z ekosystemów wodnych, np. ścieków.

Słowa kluczowe: szkła wodne sodowe, badania turbidymetryczne, sole niklu, ekosystemy wodne

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Natalia KUTSEVOL[1], Mykola BEZUGLYI
and Valentina VYSOTSKA

FLOCCULATION PROPERTIES OF DEXTRAN-*graft*-POLYACRYLAMIDE OF VARIOUS INTERNAL STRUCTURE

WŁAŚCIWOŚCI FLOKULACYJNE DEKSTRANU-*graft*-POLIAKRYLOAMIDOWEGO O RÓŻNYCH STRUKTURACH WEWNĘTRZNYCH

Abstract: Two series of Dextran-*graft*-Polyacrylamide copolymers (D-*g*-PAA) with polysaccharide backbone having different molecular weights (M_w = 20 000 and M_w = 70 000) and with 5, 10, 15 or 20 PAA-grafts per one Dextran macromolecule were tested as flocculation aids in the model kaolin suspensions. These copolymers have shown high flocculation efficiency significantly dependent upon their internal structure. The flocculation ability of D-*g*-PAA samples with the same number of PAA-grafts inversely relates to the spacing of the grafts (ie the length of backbone between the grafts).

Keywords: dextran, polyacrylamide, graft copolymers, flocculation, kaolin suspension

It is well known that Polyacrylamide flocculants in non-ionic, cationic and anionic form are widely used in wastewater treatment [1]. The flocculation performance of flocculants depends on the chemical nature of flocculants, their molecular weight, the suspension solid content in the wastewater, etc [2]. The solution properties of polymer-flocculant have strong influence on the flocculation process, namely, the more expanded polymer chain, the better its flocculation ability. The shape of polymer chain in solution mainly depends on the concentration of the linear polymer in solution for given polymer/solvent system [3]. But for polymers of non-linear architecture the number of variable parameters become overwhelmingly large, namely, initial polymer architecture, average degree of polymerization, solubility properties, changing the solvent composition, distance between grafts, nature and flexibility of backbone and grafts, etc [4–7]. All these factors can influence the formation of nanostructure,

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[1] Department of Chemistry, National Taras Shevchenko University, 60 Volodymyrska str., Kyiv 01033, Ukraine, tel. +38 044 239 34 11, email: kutsevol@ukr.net

determining the final properties of such compounds. We synthesized non-linear biohybrid water-soluble polymers of controlled nanostructure by grafting of synthetic polymers Polyacrylamide onto Polysaccharide backbone. It seems to be a promising approach for obtaining polymers with non-linear architecture, namely, spherical polymer brushes [8], containing Polyacrylamide corona.

This study is aimed to investigate the effect of internal structure of Dextran-*graft*-Polyacrylamide (D-*g*-PAA) on its flocculation efficiency in kaolin polydisperse suspension for optimization of the fine particle setting.

Materials and methods

Two series of Polyacrylamide grafted to Dextran backbone copolymers (M_w = 20 000 and M_w = 70 000), designated as D20-*g*-PAA and D70-*g*-PAA correspondingly, were synthesised by radical polymerization using Ce(IV)/HNO_3 redox system. Dextrans were purchased from Serva (Sweden), Cerium (IV) ammonium nitrate from Aldrich (CAN), Acrylamide from Reanal (Hungary).

The average number of grafting sites per backbone molecule depends on the ratio of ceric ion concentration to dextran [9]. The ratio of mole Ce(IV) to mole Dextran was equal to 5, 10, 15 and 20. The amount of monomer Acrylamide was kept the same for all synthesis. All D-*g*-PAA copolymers were synthesized and purified according to procedures described in detail in [10].

The molecular parameters of D-*g*-PAA in water solution were determined by the static light scattering (LS) experiments carried out by using SEMATECH apparatus with laser source He-Ne of wavelength λ = 632.8 nm and the scattering angle range between 30 and 150°. Light scattering (LS) results were analyzed in terms of the excess Rayleigh ratio R(q) by using a classical Zimm-plot which yields the weight-average molar mass M_w, the z-average radius of gyration R_z and the second virial coefficient A_2 [11].

The specific viscosity [η] was determined by viscometry measurements performed for dilute solution at 25.0 ± 0.1 °C, using an Oswald type viscometer. The critical concentration C* introduced by de Gennes [12], at which the polymer coils start to overlap is expressed as:

$$C^* \quad 1/[\eta]$$

The D-g-PAA samples were tested as flocculant agents in kaolin polydisperse suspensions (3 g/dl*). Flocculation process parameters were determined for a wide range of flocculants concentrations. All procedures were strongly standardized and carried out as described in [13]. Polymer solution was added in a single step to a cylinder with kaolin powder and mixed by moving a cylinder up and down six times to ensure that the suspension was well homogenized and the dispersion level was visually checked. All tests were carried out at 20 °C. The initial settling rates of

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* 1 dl = 0.1 dm^3

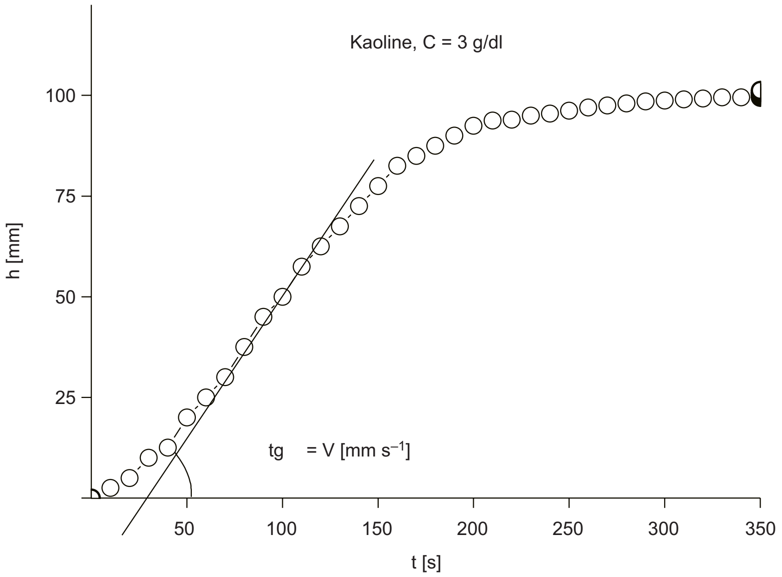

Fig. 1. Typical kinetic curve of flocculation process

flocculated suspension were determined by recording the time taken for the "mud line" (solid-liquid interface) in the 50 cm^3 cylinder. The typical kinetic curve of polymer--induced flocculation process is shown in Fig. 1. Using this curve the suspension sedimentation rate was estimated. In 20 minutes after treatment with dose of the flocculants the optical density (A_{540}) of supernatant liquid was determined by spectrometer at $\lambda = 540$ nm. It was the characteristic of supernatant clarification.

Results and discussion

The copolymers of D20-*g*-PAA and D70-*g*-PAA series have theoretically 5, 10, 15 or 20 PAA-grafts per Dextran backbone in accordance with the synthesis conditions. All copolymers have high molecular masses but $M_{\mathrm{wD}\text{-}g\text{-}\mathrm{PAA,5grafts}} > M_{\mathrm{wD}\text{-}g\text{-}\mathrm{PAA,10grafts}} > M_{\mathrm{wD}\text{-}g\text{-}\mathrm{PAA,15grafts}} > M_{\mathrm{wD}\text{-}g\text{-}\mathrm{PAA,20grafts}}$ for both series of copolymers with D20 and D70 backbone. This is an expected result because CAN is both an initiator of copolymerization and its interrupt agent. So, the increase of its amount in system changes the balance of two opposite radical polymerization processes: growth of polymer chain and its rupture.

The molecular parameters obtained by light scattering and viscometry for different copolymers are reported in Table 1. According to the value of M_w and R_z for graft copolymers and value of M_w for individual dextrans we can assume that these copolymers are star-like. Bearing in mind that the concentrations used for LS is less than the critical "overlap" concentration C* (Table 1), the intermolecular interaction can be neglected. Thus, the molecular parameters of graft copolymers D-*g*-PAA characterize properties of individual macromolecules in water solution.

Table 1

Molecular parameters of graft copolymers determined by LS (light scattering) and viscometry in water

Sample	$M_w \cdot 10^{-6}$	A_2	R_z [nm]	R_z^2/M_w	C* [g/dl]
D20-*g*-PAA, 5 grafts	3.65	0	152	6.33	0.433
D20-*g*-PAA, 10 grafts	2.22	0	104	4.87	0.566
D20-*g*-PAA, 15 grafts	1.08	0	59	3.22	0.522
D20-*g*-PAA, 20 grafts	1.07	0	54	2.73	0.704
D70-*g*-PAA, 5 grafts	3.11	0	99	3.15	0.285
D70-*g*-PAA, 10 grafts	2.43	0	78	2.50	0.474
D70-*g*-PAA, 15 grafts	2.29	0	73	2.33	0.790
D70-*g*-PAA, 20 grafts	0.96	0	55	3.15	1.188

The values of the radii of gyration (R_z) define the extended conformation of copolymer macromolecules in solution. In spite of zero values of the second virial coefficient A_2 the copolymers of both series are characterized by high value of R_z, especially for D20-*g*-PAA and D70-*g*-PAA with 5 grafts per Dextran macromolecule. The important characteristic for nonlinear polymers is the “factor of compactness” that is expressed as R^2/M [14]. While compare the samples of D70-PAA copolymers with D20-PAA ones having close molecular mass and equal number of grafts, we found the values of R^2/M for D20-*g*-PAA copolymers are higher (Table 1), therefore their compactness is lower. This data is in good agreement with our previous results on copolymer intramolecular structure [10]. X-Ray diffraction experiments have shown that in case of D20-PAA the scattering curve resembles closely that of a worm-like chain. For D70-PAA, the behaviour differs from that of a worm-like chain, although it is definitely not random, namely the PAA chains may be highly extended near their tethering point and recover a random conformation far from this point. So the PAA chains of D20-PAA with a closer spacing between grafts have a more linear and therefore more expanded conformation than those of D70-*g*-PAA (Fig. 2). Thus, the internal structure of D-*g*-PAA copolymers is dependent upon the distance between grafts and the length of PAA-chains.

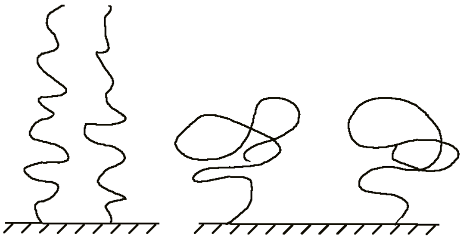

Fig. 2. Scheme of copolymer fragment near tethering points

According to experimental results the flocculation activity of copolymers was revealed to be very high (Table 2). The values of C* (Table 1) testify that the polymer solutions used in flocculation process are very dilute and, thus, an analysis the flocculation parameters using the molecular parameters of copolymers obtained by LS (Table 1) is correct.

Table 2

Floc sedimentation rate in kaolin suspensions (C = 3 g/dl)

Samples	D70-PAA 5 grafts	D70-PAA 15 grafts	D70-PAA 20 grafts	D20-PAA 5 grafts	D20-PAA 15 grafts	D20-PAA 20 grafts
C [g/dl]	V [mm/s]					
0	0.80	0.80	0.80	0.80	0.80	0.80
0.00001	0.87	0.75	0.75	0.84	0.84	0.86
0.00005	1.38	1.1	1.3	1.56	0.85	1.20
0.0001	1.63	1.42	1.5	1.87	1.01	1.42
0.0005	2.25	2.15	1.97	3.75	1.62	1.60
0.001	3.00	2.50	2.25	4.12	1.97	1.95
0.005	3.50	2.75	2.75	4.30	2.37	2.80
0.01	3.75	3.05	2.8	4.62	2.4	2.90

Polymer-induced flocculation of mineral suspensions is complicated process that involves many steps, namely mixing of polymer molecules among the particles; adsorption of polymer chains on the particles; rearrangement of the adsorbed chains; collisions between polymer-adsorbed particles; and flock formation and also break-up of flocks [15]. It is impossible to single out each step of this process in our investigation but the analysis of flocculation parameters permits to find the relationship between the internal structure and the flocculation efficiency of examined copolymers.

The suspension sedimentation rate (V) that is the kinetic characteristic of flocculation process depends on flocculant dose (Table 2). Flocculant creates bridges between kaolin particles that causes the formation of flocks and their setting. The dimensions of flocks are in direct dependence on flocculant concentrations.

As it resulted from experimental data sedimentation rate is the greatest for samples with the highest values of macromolecular mass and the highest values of R^2/M parameter (less compactness). It is more interesting to compare the samples with close M_w, for instance D20-*g*-PAA, 15 grafts and D20-*g*-PAA, 20 grafts. The kinetic characteristics, namely V, are essentially different in spite of fact that M_w are $1.08 \cdot 10^6$ and $1.07 \cdot 10^6$ respectively. The reason for better effectiveness of the sample D20-*g*-PAA, 15 grafts is the more extended conformation of their macromolecules in water solution (the "factor of compactness" R^2/M is greater than for D20-*g*-PAA, 20 grafts). So the internal structure of D-*g*-PAA copolymers which defines the macromolecule conformation in water solution is very important for flocculation performance.

The degree of water clarification that was estimated by optical density after 20 minutes after treatment with flocculant agent revealed to be greater and the dose can be less when D-*g*-PAA copolymers with 5 PAA-grafts were used (Table 3). Expanded structure of these copolymers allows them to capture much more solid particles including very small ones.

Table 3

Optical density of supernatant liquid

Sample	D70-PAA 5 grafts	D70-PAA 15 grafts	D70-PAA 20 grafts	D20-PAA 5 grafts	D20-PAA 15 grafts	D20-PAA 20 grafts
C [g/dl]	A_{540}					
0	1.222	1.222	1.222	1.222	1.222	1.222
0.00001	1.117	1.216	1.200	0.909	1.205	1.146
0.00005	1.061	0.826	1.144	0.812	1.208	1.104
0.0001	0.840	0.803	0.735	0.579	1.118	1.098
0.0005	0.507	0.578	0.392	0.431	0.634	0.621
0.001	0.495	0.362	0.376	0.327	0.577	0.461
0.005	0.211	0.262	0.199	0.100	0.291	0.279
0.01	0.121	0.177	0.154	0.078	0.251	0.190

When compare the flocculation efficiency of D20-*g*-PAA and D70-*g*-PAA (Fig. 3a, b) anyone can be convinced of the fact that the flocculation ability is inversely related to the spacing of the PAA grafts (ie the length of backbone between the grafts). Thus, for D20-*g*-PAA and D70-*g*-PAA having 5 grafts per macromolecule ($c = 1 \cdot 10^{-2}$ g/dl) the sedimentation rates are 4.62 and 2.88 mm/s and values of optical density are 0.078 and 0.121, respectively. Due to more expanded conformation in water solution the sample of D20-*g*-PAA, 5 grafts is more effective flocculant than D70-*g*-PAA, 5 grafts which has greater distances between grafts and therefore less extended structure.

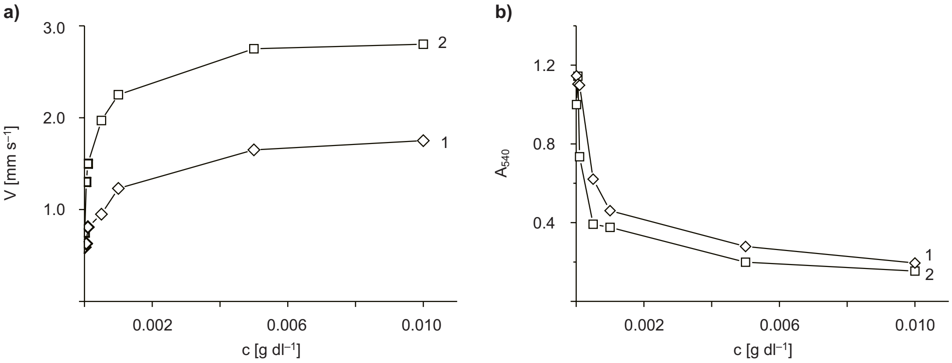

Fig. 3. Suspension sedimentation rate (a) and optical density of supernatant (b) for D70-PAA, 5 grafts (1) and D20-PAA, 5 grafts (2) copolymers

Thus the analysis of flocculation process parameters kinetic and the degree of water clarification has shown that the flocculation efficiency depends on macromolecular conformation directly. When the internal structure of grafted copolymer ensures the expanded macromolecular conformation in water solution the functional groups of these copolymers are capable to capture pollutants and flocculation process will pass quickly and with high degree of clarification.

Conclusions

The internal structure of branched D-*g*-PAA macromolecules has influence upon the properties of their aqueous solutions. In kaolin suspensions the best flocculation efficiency was registered for copolymers with shorter distance between tethering points. Thus, the conformation of PAA grafts in star-like copolymers D-*g*-PAA, which according to the theoretical model are the spherical brushes with PAA-corona, as well as the copolymer compactness in solution plays a predominant role in the flocculation process.

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WŁAŚCIWOŚCI FLOKULACYJNE DEKSTRANU-*graft*-POLIAKRYLOAMIDOWEGO O RÓŻNYCH STRUKTURACH WEWNĘTRZNYCH

Abstrakt: Badano właściwości flokulacyjne kopolimerów dekstran-*graft*-poliakryloamidowych (DG-PAA) ze szkieletem dekstranowym o dwóch różnych masach molekularnych (M_w = 20 000 i M_w = 70 000) oraz z 5, 10, 15 lub 20 molekułami PAA dołączonymi (zaszczepionymi) do tego makromolekularnego szkieletu. Do pomiarów wykorzystywano zawiesinę kaolinu w wodzie. Kopolimery te miały dużą skuteczność flokulacyjną zależną od ich struktury molekularnej. Zdolność flokulacyjna próbek D-*g*-PAA, z taką samą liczbą zaszczepionych molekuł PAA, jest odwrotnie proporcjonalna do odległości między molekułami zaszczepionymi do szkieletu molekuły dekstranu.

Słowa kluczowe: dekstran, poliakryloamid, kopolimery szczepione, flokulacja, zawiesina kaolinu

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Lech SMOCZYŃSKI[1], Kamilla T. DŁUŻYŃSKA[1],
Bogusław PIEROŻYŃSKI[1], Regina WARDZYŃSKA[1],
Beata ZAŁĘSKA-CHRÓST[1]
and Anna A. ZABOROWSKA-PIWOROWICZ[1]

MECHANISM OF P-PO_4 REMOVAL FROM CHEMICALLY TREATED WASTEWATER

MECHANIZM USUWANIA P-PO_4 ZE ŚCIEKÓW OCZYSZCZANYCH CHEMICZNIE

Abstract: The coagulation-flocculation of model wastewater was studied to compare the coagulation performance of PAC, $Al_2(SO_4)_3$ and PIX. The proposed hypothesis that the amount of a coagulant has to be precisely determined based on the condition of the minimum of the parabola dx = 0 was confirmed for aluminium coagulants. It was found that the dose of PIX should be calculated using the coordinates of the point of intersection of appropriate straight lines. Then the mechanism of phosphorus removal from model wastewater was examined under conditions of the optimum (constant) coagulant dose. The Al:P molar ratio obtained in the study enabled to exclude the possibility of chemical precipitation of any aluminium orthophosphate. The determination coefficient R^2 for a converted equation of the Langmuir adsorption isotherm indicated chemical nature of orthophosphate (adsorbate) binding by colloidal micelles of $Al\{OH\}_3$ and $Fe\{OH\}_3$ (adsorbent). Finally, the adsorption equilibrium constant and maximum adsorption capacity were suggested for the sorption process under consideration.

Keywords: wastewater treatment, coagulation, inorganic chemicals, phosphate, COD

The main stages of chemical coagulation are: a) destabilization of the colloidal system, b) aggregation and flocculation. Destabilization is most often caused by ions or colloidal particles, referred to as coagulants [1, 2], whose charge is opposite to the surface charge stabilizing eg a sol. Aggregation-flocculation may be generally described as a process in which particles coagulated during latent coagulation combine to form bigger agglomerates-flocs [3].

In the process of wastewater coagulation-flocculation the key problem is the choice of a coagulant and precise determination of its optimum dose [4]. Coagulant deficiency may significantly impair coagulation [5–7], while an excess of coagulant (overdosing)

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[1] Departament of Chemistry, University of Warmia and Mazury in Olsztyn, pl. Łódzki 4, 10–957 Olsztyn, email: lechs@uwm.edu.pl, kamilla.munska@uwm.edu.pl

may lead not only to the loss of coagulating properties, but also to sol overload [8] as well as to the release of pollutants coagulated (absorbed) under conditions of an optimum coagulant dose. Theoretically, under optimal conditions, the zeta potential ξ of the coagulated system should be equal to 0. However, practice often shows that maximal pollutant removal, eg from chemically coagulated wastewater, is not reached at $\xi = 0$ [5]. Therefore, the jar-test procedure is still widely applied, since it permits precise determination of the optimal coagulant dose [9, 10].

In wastewater treatment technology much attention is paid to the efficiency of chemical removal (also called precipitation) of eutrophicating phosphorus with the use of iron(III) and aluminum cations contained in the most commonly applied inorganic coagulants, ie PIX and alum [11, 12]. A stoichiometric analysis shows that the molar ratio of Fe(Al) : P (the number of moles Fe or Al per mole P) higher than 3 : 1 [11, 13], at a final pH of the system below 5, practically excludes the possibility of precipitation of $AlPO_4$ or $(AlOH)_3(PO_4)_2$. The probability of formation of final form $[Al(OH)_2]_3PO_4$ is very low, during this chemical step. On the other hand, the solubility of $Al_2(HPO_4)_3$, and especially of $Al(H_2PO_4)_3$, is so high that it excludes the possibility of P-PO_4 removal in this form, as a sludge component.

It follows that phosphorus removal from chemically coagulated wastewater may be interpreted in a different way. It seems that this process is a result of sorption of orthophosphate PO_4^{3-} anions on positively charged particles of $\{Fe(OH)_3\}$ or $\{Al(OH)_3\}$, constituting a colloidal sorbent [14]. Therefore, the main aim of this study, apart from presenting a new concept for determining an optimum coagulant dose, was to explain the mechanism of phosphate phosphorus removal from wastewater coagulated with standard inorganic coagulants, such as PIX, alum and PAC.

Material and methods

The study was conducted on model wastewater obtained by dissolving a constant, precisely weighed analytical sample of milk powder (NESTLE) in 2000 cm^3 of the solution. Accurately measured 200 cm^3 of newly prepared wastewater was transferred into ten beakers. A very precise method was employed in the study: small amounts of a concentrated solution of inorganic coagulant were added to an adequate volume of model wastewater, using a glass pipette. The coagulant was dosed as follows:

– beaker 1 = 0 drops of a coagulant,
– beaker 2 = 1 drop of a coagulant,
– beaker 3 = 2 drops of a coagulant, etc.

The coagulant and wastewater were mixed rapidly for approx. 30 s. Then, following 15 minute sedimentation, 2 cm^3 samples were taken accurately with a pipette from above the surface of the sludge for analysis and physicochemical measurements. Chemical oxygen demand (COD), total phosphorus, turbidity, suspended solids and pH were determined by standard methods [15, 16].

The measurement of the volume of 100 drops of a given coagulant as well as all coagulation-flocculation tests for each coagulant were performed in seven repetitions, disregarding two highest and two lowest values. Arithmetic means and standard deviations, calculated based on three remaining values, are presented in tables and figures. Such a procedure permitted accurate determination of the volume of a single drop of a given coagulant as well as of the cation dose used in the experiment.

Values of 100 drops volume and COD, total phosphorus, suspended solids and turbidity of crude wastewater, with standard deviations, are given in Table 1.

Table 1

Characteristics of coagulants and raw wastewater

Coagulant Parameter	PAC	$Al2(SO_4)_3$	PIX	Mean standard deviation
Coagulant amount [mg Al/Fe dm^3] in 1 drop	30.70 ± 0	8.66 ± 0	37.68 ± 0	0
$mg \cdot dm^{-3}$				
COD	12450 ± 1278	13912 ± 85.4	12780 ± 503	767
Phosphorus	82 ± 10.4	76 ± 10.8	53 ± 10.4	15.2
Turbidity	96 ± 2.61	98 ± 3.16	119 ± 4.5	12.8
Suspended Solids	85 ± 3.46	93 ± 6.8	85 ± 3.9	4.48
100 drops	4.1 cm^{-3} ± 0.0	4.33 cm^{-3} ± 0.0	3.68 cm^{-3} ± 0.0	0.0

The following inorganic coagulants were used:

a) PAC – produced by DEMPOL-ECO in the form of an aqueous light-gray solution, density: 1.28 $g \cdot cm^{-3}$ at 293 K, chemical composition: 20.68 % of Al_2O_3, 6.5 % of Cl^- and 0.02 % of Fe,

b) $Al_2(SO_4)_3$ – obtained at the laboratory by dissolving 61.70 g of $Al_2(SO_4)_3 \cdot 18H_2O$ in 250 cm^3 of the solution,

c) PIX 113 – produced by KEMIPOL in the form of a dark-brown 41 % solution, chemical formula: ≈ $Fe_2(SO_4)_3$, density: 1.55 $g \cdot cm^{-3}$ in 293 K, chemical composition: 11.8 % of Fe^{3+} and 0.45 % of Fe^{2+}.

At the next stage of the experiment, a KH_2PO_4 solution obtained by dissolving 21.95 g of this salt in 250 cm^3 of the solution was added to ten beakers containing 200 cm^3 of model wastewater, in the following amount:

– beaker 1–0.5 cm^3 of a working solution of KH_2PO_4 , ie 10 mg of P,

– beaker 2–1.0 cm^3 of KH_2PO_4 = 20 mg of P,

– beaker 3–1.5 cm^3 of KH_2PO_4 = 30 mg of P, etc.

Then the constant optimum dose of a given coagulant was added to each beaker, ie a) PAC – 150.0 mg $Al \cdot dm^{-3}$, b) $Al_2(SO_4)_3$ – 56.3 mg $Al \cdot dm^{-3}$, c) PIX – 75.4 mg $Fe \cdot dm^{-3}$. Next wastewater samples were mixed rapidly with KH_2PO_4 and a coagulant, and after 15 minute sedimentation the above sampling procedure was repeated. The phosphorus test was conducted in seven replications for each coagulant, again disregarding two highest and lowest values.

Regression of the ratio between adsorbed phosphorus and equilibrium amount of phosphorus, Pa = f(Pe), was analyzed for the converted Langmuir and Freundlich isotherm models. The transformed dependences had the following mathematical form:

a) Langmuir isotherm: $$\frac{[P_e]}{[P_a]} \quad \frac{1}{a_m \cdot K} \quad \frac{1}{a_m} \cdot [P_e] \qquad (1)$$

where: $[P_e]$ = concentration of equilibrium phosphorus; $[P_a]$ = concentration of adsorbed phosphorus; a_m = maximum adsorption capacity; K = adsorption equilibrium constant.

b) Freundlich isotherm: $$\lg [P_a] = \lg K + n \cdot \lg [P_e] \qquad (2)$$

where: $[P_e]$ = concentration of equilibrium phosphorus; $[P_a]$ = concentration of adsorbed phosphorus; K, n = the constants of the Freundlich equation.

An equation of a straight line (the upper right corner in figures) and the value of the determination coefficient R^2 were determined for each of the tested isotherms.

Results and discussion

Figure 1 presents changes in the pH of model wastewater coagulated with PAC, $Al_2(SO_4)_3$ and PIX.

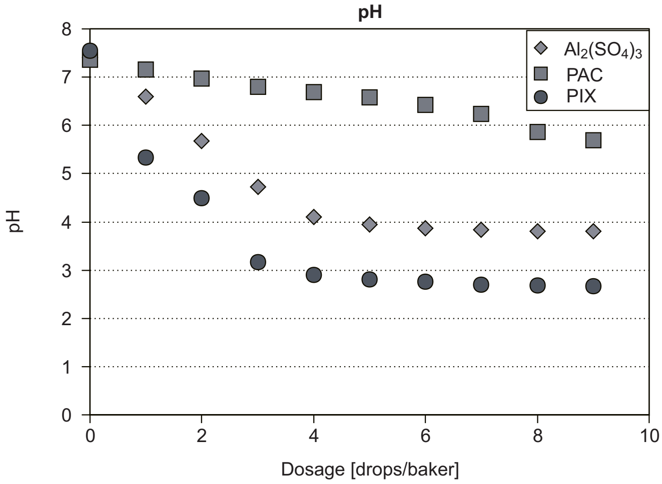

Fig. 1. Changes in the pH of model wastewater coagulated with PAC, $Al_2(SO_4)_3$ and PIX

An increase in the coagulant dose caused a decrease in the pH of model wastewater having lower buffering capacity compare with sewage for instance. The decrease in pH resulted from the hydrolysis of aluminium salts or iron(III) salts. Primary hydrolyzed PAC, with a [OH]/[Al] ratio > 2, except for two extremely high doses, ensured a pH close to neutral in the coagulated system. Under conditions considered optimal at the subsequent stages of the study, pH was ≈ 3.0–4.5 for PIX, whereas for both the optimal and extreme doses of $Al_2(SO_4)_3$ the reaction remained at a relatively stable level, ie pH ≈ 4.0. Higher doses of PIX reduced the reaction to pH < 3. Changes in pH levels may be related to higher efficiency of condensation, polycondensation and polymerization of hydroxy aluminium cations, compared with hydroxy iron cations [17], resulting from an increase in coagulant concentration. The possibility of forming polycations of the following types: $[Al_2(OH)_2]^{4+}$, $[Al_3(OH)_4]^{5+}$, $[Al_6(OH)_{12}]^{6+}$ or "$\{Al_{13}...\}^{7+}$" [18, 19] reduces the proton-forming capacity of hydrolysis of aluminium coagulants, in comparison with the proton-forming capacity of hydrolysis of Fe^{3+} cations. The fact that the so-called zero-point-of-charge of $Fe(OH)_3$ and $Al(OH)_3$ occurs at pH ≈ 8.5 and pH ≈ 5.0, respectively [20], may confirm the greater ability of aluminum coagulants to produce various polymeric forms within the pH ≈ 4.0–4.5 range, compared with iron coagulants. Low pH values of the coagulated system usually contribute to the neutralization of the negatively charged surfaces of wastewater colloids, leading to their destabilization. However, the significance of this phenomenon should not be overestimated, since not all wastewater pollutants have the colloidal form, and their removal is often related to other processes accompanying coagulation-flocculation, such as precipitation, sorption, etc. It follows that acidification of coagulated wastewater may disturb sorption or increase the solubility of newly-formed sludge.

A. Modeling in wastewater coagulation

Figures 2–4 show turbidity, suspended solids, total phosphorus and COD removal from model wastewater, coagulated with PAC, $Al_2(SO_4)_3$ and PIX. In the case of PIX, turbidity decreased substantially following the application of the first two doses. This was not a typical parabolic distribution, as confirmed by the low value of the calculated coefficient $R^2 = 0.6132$ for a quadratic regression equation. Therefore, the results obtained with PIX (Fig. 4) are presented in the form of two intersecting straight lines. The x coordinate of the intersection point of these two straight lines represents the optimal dose of PIX.

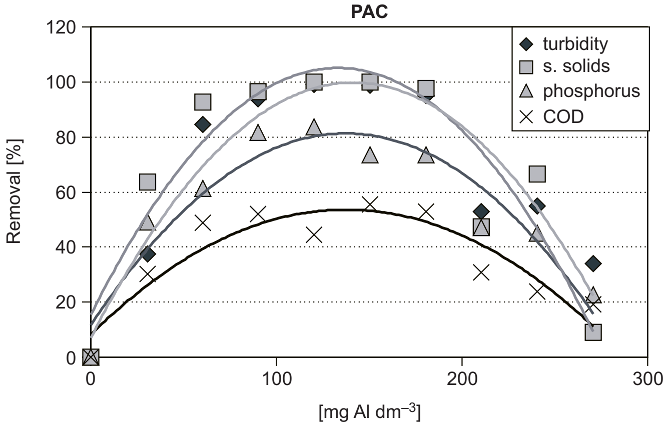

Fig. 2. Turbidity, suspended solids, phosphorus, COD removal from model wastewater coagulated with PAC

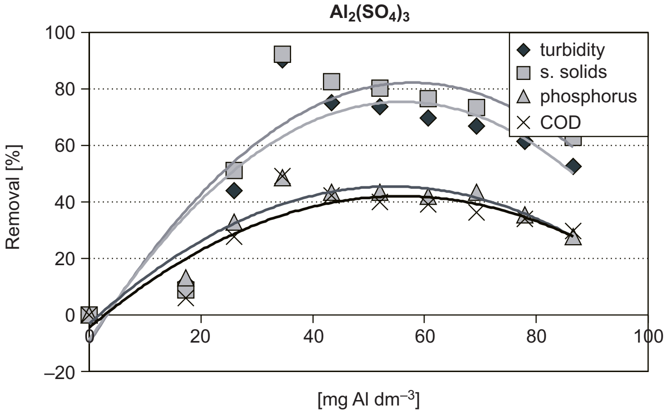

Fig. 3. Turbidity, suspended solids, phosphorus, COD removal from model wastewater coagulated with $Al_2(SO)_4$

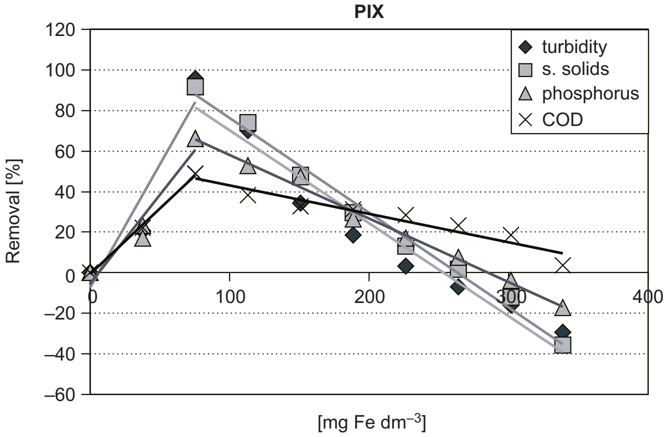

Fig. 4. Turbidity, suspended solids, phosphorus, COD removal from model wastewater coagulated with PIX

In every cases PAC was found to be the most effective. PAC was followed by PIX. Exceeding the optimum dose of all coagulants caused a gradual increase in all parameters. The effect of coagulant overdosing on parameters removal was particularly noticeable in the case of PIX, whose maximum dose resulted in the exceeding of the initial value of turbidity, suspended solids, phosphorus. This could be caused eg by colloid overload, leading to: a) undesirable hydrosol restabilization, which in the case of PIX probably increases sol concentration by incorporating a part of colloidally dispersed $\{Fe(OH)_3\}$, b) partial peptization of the already formed gel/sludge. The lowest increase in parameters was recorded for wastewater coagulated with an excess of $Al_2(SO_4)_3$. Taking into account a constant level of pH ≈ 4.0 (Fig. 1) in this group of coagulated wastewater samples, the above processes a) and b) for the products of $Al_2(SO_4)_3$ hydrolysis may be disregarded, and a slight increase in parameters may be a consequence of a certain increase in the concentration of dispersed phase coming from not completely destabilized $\{Al(OH)_3\}$. At pH ≈ 2.7–3.0 and pH ≈ 5.8–7.0 the products of hydrolysis of PIX and PAC, respectively (Fig. 1), are destabilized less effectively and considerably increase the concentration of dispersed phase as well as the all parameters of coagulated wastewater. Overdosing of $Al_2(SO_4)_3$ decreased COD removal efficiency by about 13 % only and turbidity, suspended solids, phosphorus removal was still from about 20 % to 60 %, even when the maximum dose of this coagulant was applied. Phosphorus removal by $Al_2(SO_4)_3$ was at a comparable level within a relatively wide range of coagulant concentrations (43 to 69 mg of Al · dm^{-3}). Such a wide range of effective coagulation could be related to pH ≈ 4.0, which was rather stable for these amounts of $Al_2(SO_4)_3$. All of the above relationships indicate that an increase in coagulant dose was more less accompanied by an increase in the phosphorus content of wastewater. Except for PAC, an increase in coagulant dose > "4 drops" led to the activation of phosphate ions in coagulated wastewater, despite the stabilization of the system pH (Fig. 1). This increase may be explained in terms of increasing mobility of protonated orthophosphates or other species undergoing transformation of the following types:

$$[Al(OH)_2]_3PO_4 \rightarrow (AlOH)_3(PO_4)_2 \rightarrow AlPO_4 \rightarrow Al_2(HPO_4)_3 \rightarrow Al(H_2PO_4)_3 \quad (3)$$

$$[Fe(OH)_2]_3PO_4 \rightarrow (FeOH)_3(PO_4)_2 \rightarrow FePO_4 \rightarrow Fe_2(HPO_4)_3 \rightarrow Fe(H_2PO_4)_3 \quad (4)$$

Taking into consideration some changes among the above forms enables to propose the following equations of reactions occurring in the analyzed wastewater and in sludge treated with excess Al^{3+} or Fe^{3+} ions:

$$3AlPO_4 + Al_2(SO_4)_3 + 3H_2O \rightarrow Al_2(HPO_4)_3 + 3AlOHSO_4 \quad (5)$$

$$3FePO_4 + Fe_2(SO_4)_3 + 3H_2O \rightarrow Fe_2(HPO_4)_3 + 3FeOHSO_4 \quad (6)$$

where $AlPO_4$ or $FePO_4$ is much less soluble than $Al_2(HPO_4)_3$ or $Fe_2(HPO_4)_3$.

Simultaneously, hydrogen ions formed during these reactions and hydrogen ions introduced with excess acid coagulant may cause the following changes:

$$3AlPO_4 + 2H_3O^+ \rightarrow Al_2(HPO_4)_3 + Al(OH)^{2+} \quad (7)$$

$$3FePO_4 + 2H_3O^+ \rightarrow Fe_2(HPO_4)_3 + Fe(OH)^{2+} \quad (8)$$

The above diagrams showing the direction of changes explain the experimentally confirmed fact that an overdose of inorganic coagulant has a negative effect on phosphate removal from chemically coagulated wastewater.

The easily noticeable correlation between the pattern of changes in turbidity and suspended solids and the dependence of chemical oxygen demand on inorganic coagulant dose, presented above, suggests that organic substances constituted colloidal dispersed phase in the analyzed wastewater. The mechanism of destabilization of this sol/suspension was most probably based primarily on the neutralization of the negative surface charge by: a) iron or aluminum hydroxy cations or polycations as well as positively charged micelles of $\{Fe(OH)_3\}$ or $\{Al(OH)_3\}$, respectively; b) H^+ ions formed during hydrolysis of the inorganic coagulants used in the study. Processes a) led to aggregation, agglomeration, flocculation and sedimentation of sludge. At the stage of aggregation the mixture of positively charged hydroxy cations, polycations and micelles constituted a colloidal sorbent that permitted effective "trapping" of phosphates as well as $P\text{-}PO_4$ removal from the liquid phase of the treated wastewater. If such a mechanism of the observed changes is assumed, both the behavior of PIX, in relation to PAC and $Al_2(SO_4)_3$, and the differences in the optimal dose of aluminium coagulants, seem to be easy to explain. Under conditions of the optimal dose of PIX, pH = 3.0–4.5 (Fig. 1) ensured over ten-fold and over hundred-fold higher $[H^+]$ than with the use of $Al_2(SO_4)_3$ and PAC, respectively. The fact that the so-called zero-point-of-charge [26] of $Fe(OH)_3$ and $Al(OH)_3$ occurs at $pH \approx 8.5$ and $pH \approx 5.0$, respectively, indicates that pH=3.0–4.5 (PIX) provides a much higher positive surface charge to the $\{Fe(OH)_3\}$ micelle than pH = 4.0–7.0 to $\{Al(OH)_3\}$ micelles. It follows that already the "second drop" of PIX constituted the optimal dose of this coagulant, while in the case of PAC and $Al_2(SO_4)_3$ four or five drops were needed.

Table 2

Regression equations and determination coefficients R^2

Parameter	PAC	$Al_2(SO_4)_3$	PIX
Suspended solids	$y = 0.0043x^2 - 1.1465x + 71.935$ $\underline{R^2 = 0.8624}$	$y = 0.0258x^2 - 2.9787x + 102.7$ $\underline{R^2 = 0.8145}$	1) $y_1 = -1.0377x + 91.567$ $\underline{R_1^2 = 0.9263}$ 2) $y_2 = 0.3977 - 19.671$ $\underline{R_2^2 = 0.9894}$
Turbidity	$y = 0.0045x^2 - 1.2641x + 89.546$ $\underline{R^2 = 0.8951}$	$y = 0.0269x^2 - 2.9784x + 106.06$ $\underline{R^2 = 0.8039}$	1) $y_1 = -1.5127x + 130.2$ $\underline{R_1^2 = 0.9028}$ 2) $y_2 = 0.5451x - 18.86$ $\underline{R_2^2 = 0.944}$
Phosphorus	$y = 0.003x^2 - 0.8277 + 2.175$ $\underline{R^2 = 0.9002}$	$y = 0.0127x^2 - 1.3704x + 78.421$ $\underline{R^2 = 0.8039}$	1) $y_1 = -0.4644x + 55.833$ $\underline{R_1^2 = 0.9271}$ 2) $y_2 = 0.1662x + 5.5595$ $\underline{R_2^2 = 0.9921}$
COD	$y = 0.2984x^2 - 82.063x + 11420$ $\underline{R^2 = 0.8413}$	$y = 2.0868x^2 - 232.55x + 14544$ $\underline{R^2 = 0.805}$	1) $y_1 = -82.803x + 12880$ $\underline{R_1^2 = 0.9968}$ 2) $y_2 = 17.917x + 5470.6$ $\underline{R_2^2 = 0.9232}$

Table 2 presents second degree regression equations (parabolas) and determination coefficients R^2 for changes in turbidity, suspended solids, total phosphorus and COD. The optimum doses of PAC, $Al_2(SO_4)_3$ were determined based on the condition of the minimum of the parabola df(x) = 0, while the optimum dose of PIX was determined using the x coordinate of the point of intersection of appropriate straight lines, since this procedure provided the maximum value of the determination coefficient R^2. Then a mean value was calculated from the above four optimum doses (for turbidity, suspended solids, total phosphorus and COD). This mean value was considered to be the optimum dose of a given coagulant. The optimum doses (± standard deviations) as well as the coefficients of correlation between turbidity and suspended solids, COD and total phosphorus, are given in Table 3. Tables 4 to 7 show the values f(x), calculated based on respective regression equations. In order to better illustrate the coagulation-flocculation process, removal efficiency is given in [mg dm^{-3}] and in [%], whereas coagulant efficiency is expressed as mg of removed quantity of removed parameter per mg of coagulant.

Table 3

Mean optimum coagulant doses

Coagulant	COD	Turbidity	Suspended solids	Phosphorus	Mean	SD	Correlation	
							T:S	C:P
	mg · dm^{-3}							
PAC	138	140	133	138	137	2.97	0.940	0.945
$Al_2(SO_4)_3$	55.7	55.4	57.5	53.9	55.6	1.48	0.994	0.979
PIX	73.6	77.5	72.43	79.7	75.8	3.38	0.986	0.904

The data in Table 3 show that there are certain differences between the optimum coagulant doses for particular parameters. The greatest differences were recorded for PIX, whose doses ranged from 72.43 to 79.7 mg · dm^{-3}, while the smallest differences were noted for $Al_2(SO_4)_3$ whose doses varied from 54 to 57.5 mg · dm^{-3}. Table 3 presents also the correlations between mean values of turbidity and suspended solids as well as between COD and phosphorus for particular coagulants. The coefficient of correlation between turbidity and suspended solids was the highest for PIX (0.986) and the lowest for PAC (0.940). The correlation between COD and phosphorus was comparable for all coagulants (0.945). The high coefficients of correlation, higher than 0.940, confirm the correctness of the new concept/method for determining the optimum coagulant dose based on parabolic equations, proposed in this study.

Table 4

Turbidity at the optimum coagulant dose

Coagulant	Optimum coagulant dose [mg Al^{3+} or Fe^{3+} · dm^{-3}]	Turbidity at the mean coagulant dose [mg · dm^{-3}]	Turbidity removal [mg · dm^{-3}]	Turbidity removal [%]	Coagulant efficiency [mg turbidity per mg Al or mg Fe]
PAC	150	1.21	95.2	98.8	0.63
$Al_2(SO_4)_3$	56.3	23.6	74.4	75.9	1.32
PIX	75.4	19.21	100.2	83.9	1.33

Table 5

Suspended solids at the optimum coagulant dose

Coagulant	Optimum coagulant dose [mg Al^{3+} or $Fe^{3+} \cdot dm^{-3}$]	Suspended solids at the mean coagulant dose [$mg \cdot dm^{-3}$]	Suspended solids removal [$mg \cdot dm^{-3}$]	Suspended solids removal [%]	Coagulant efficiency [mg suspended solids per mg Al or mg Fe]
PAC	150	–3.24	88.2	103.8	0.58
$Al_2(SO_4)_3$	56.3	16.8	76.6	82	1.36
PIX	75.4	11.8	73.4	86	0.97

Table 6

Phosphates at the optimum coagulant dose

Coagulant	Optimum coagulant dose [mg Al^{3+} or $Fe^{3+} \cdot dm^{-3}$]	Phosphorus at the mean coagulant dose [$mg \cdot dm^{-3}$]	Phosphorus removal [$mg \cdot dm^{-3}$]	Phosphorus removal [%]	Coagulant efficiency [mg P per mg Al or mg Fe]
PAC	150	15.5	66.2	80.1	0.44
$Al_2(SO_4)_3$	56.3	41.5	34.5	45.4	0.61
PIX	75.4	19.5	34	63.5	0.45

Table 7

COD at the optimum coagulant dose

Coagulant	Optimum coagulant dose [mg Al^{3+} or $Fe^{3+} \cdot dm^{-3}$]	COD at the mean coagulant dose [$mg \cdot dm^{-3}$]	COD removal [$mg \cdot dm^{-3}$]	COD removal [%]	Coagulant efficiency [mg COD per mg Al or mg Fe]
PAC	150	5827	6623	53.2	44
$Al_2(SO_4)_3$	56.3	8066	5847	42	104
PIX	75.4	6730	6050	47.3	80

PAC was found to be the most effective but also the most consumed coagulant. Its efficiency could result from possibility $\{Al_{13}\}^{+7}$ [21] polycations forming, whose coagulating capacity, calculated from extrapolation of the classical Schultz-Hardy rule [22, 23] may be even 12 000-fold higher than that of simple cations Al^{3+} . In most cases the level of pollutant load removal with $Al_2(SO_4)_3$ and PIX was comparable. However $Al_2(SO_4)_3$ was characterized by the highest efficiency in mg/mg Al. PIX was less effective than PAC, but its consumption in mg Fe dm^{-3} was smaller than PAC in mg Al dm^{-3}.

B. P-PO_4 removal

The widely used Langmuir and Freundlich isotherm models, explaining the sorption mechanism, differ from each other. Therefore, the values of the determination

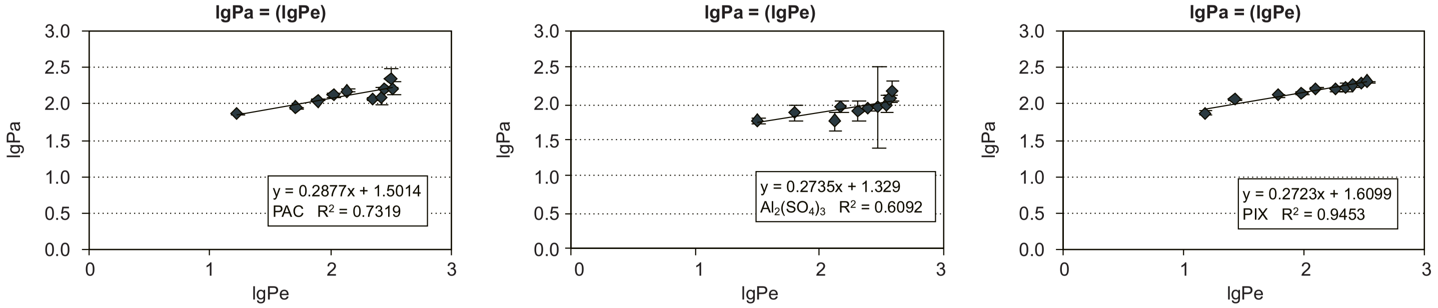

Fig. 5. Freundlich isotherms for PAC, Al$_2$(SO$_4$)$_3$ and PIX, respectively

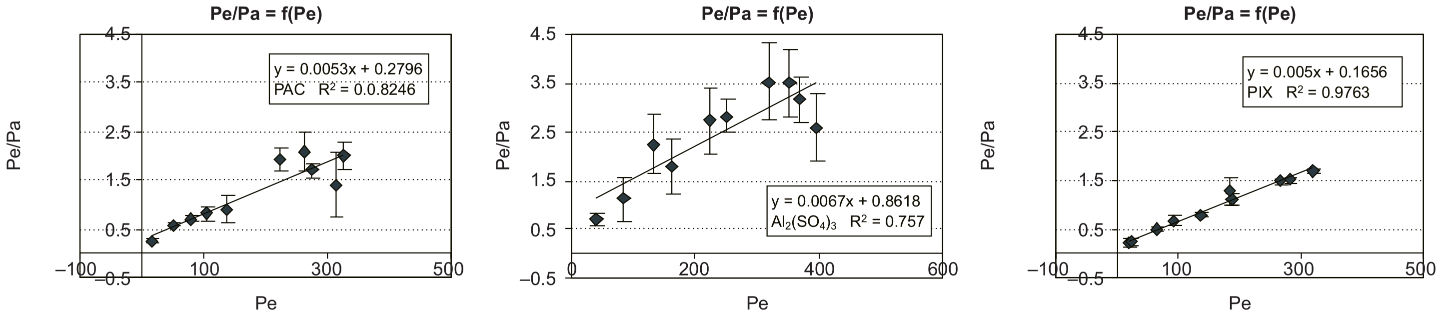

Fig. 6. Langmuir isotherms for PAC, Al$_2$(SO$_4$)$_3$ and PIX, respectively

coefficients for converted equations of straight lines, derived based on the experimental database, will not have to but may enable to choose one of these models. The results of testing the dependence Pa = f(Pe), for PAC, $Al_2(SO_4)_3$ and PIX, are shown in Figures 5, 6 and in Tables 8, 9.

Regression equations of the converted Langmuir isotherm model were characterized by significantly higher values of the determination coefficient (Figs. 5, 6). The values of the determination coefficient R^2 for the Langmuir isotherm and for the Freundlich isotherm ranged from 0.757 to 0.9763 and from 0.6092 to 0.9453, respectively. This may suggest that orthophosphates are adsorbed on colloidal sorbents, $\{Al(OH)_3\}$ and $\{Fe(OH)_3\}$, fundamentally and statistically in accordance with the Langmuir sorption model [24, 25]. According to this model, the adsorbate forms a monolayer of molecules on the adsorbent surface, which interact "vertically" with adsorption centers, but generally do not interact with one another (such interactions, if present, are weak). In addition, adsorption is limited and there is no possibility of forming a multilayer. The energy of adsorption is constant, and the adsorbent surface is homogenous in terms of energy distribution. It follows that orthophosphate sorption is of chemical nature and can be referred to as chemisorption. In this process the adsorbate particles are attached to the adsorbent surface mostly through covalent bonds, filling active centers. In this kind of sorption the chemical properties of the adsorbent and adsorbate may change at the adsorbent-adsorbate phase boundary. These properties can be also modified as a result of irreversible reactions, which means that sorption and desorption processes are not always reversible.

Table 8

Parameters and converted equations of the Langmuir isotherm model

	Equation of a straight-line Langmuir isotherm	Maximum adsorption capacity a_m [mg P per g Al or g Fe]	Adsorption equilibrium constant K
PAC	y = 0.0053x + 0.2796	188	0.019
$Al_2(SO_4)_3$	y = 0.0067x + 0.8618	149	0.0078
PIX	y = 0.005x + 0.1656	200	0.03

Maximum adsorption capacity and the adsorption equilibrium constant, being a measure of the binding energy of the sorbent-sorbate system, were determined based on the converted Langmuir isotherm equation (Table 8). PIX had the highest maximum adsorption capacity, which indicates that this coagulant was able to "trap", ie permanently adsorb, the largest amounts of orthophosphates. It does not mean, however, that PIX guarantees the highest effectiveness of phosphorus removal, since PAC was characterized by the highest degree of phosphorus removal. The lowest maximum adsorption capacity, a_m = 149 mg P per g Al, was recorded for aluminium sulfate. It should be noted that PIX had higher sorption capacity than aluminium coagulants, $a_m\{Fe(OH)_3\} > a_m\{Al(OH)_3\}$. As for the adsorption equilibrium constant, it was the highest (K = 0.03) for PIX, and the lowest (K = 0.0078) for $Al_2(SO_4)_3$. When the constant K increases, the equilibrium of the adsorption $\rightleftarrows$ desorption process shifts to the right. Low values of the constant K indicate high quality of a coagulant, able to permanently adsorb orthophosphates. In such a situation small amounts of orthophosphate ions are present in treated effluents, because they undergo only slight desorption on the sludge surface. Among the tested coagulants, $Al_2(SO_4)_3$ provided the highest level of phosphorus retention, despite the lowest maximum adsorption capacity.

Table 9

P:Al and P:Fe ratio

Ratio Coagulant	Moles P per moles Fe or moles Al	mg P per mg Al or mg Fe
PAC	1 : 6.2	1 : 5.3
$Al_2(SO_4)_3$	1 : 7.7	1 : 6.7
PIX	1 : 2.8	1 : 4.5

Phosphorus sorption by $\{Al(OH)_3\}$ and $\{Fe(OH)_3\}$ depended on the coagulant used. Table 9 presents the molar ratios of P : Al and P : Fe, ie the number of moles Al or Fe required to adsorb one mole P, as well as the corresponding weight ratios [mg]. Maximum adsorption values and the optimum coagulant dose, expressed in moles and mg, were used to calculate these ratios. The molar ratios show that there were fewer moles Fe from PIX than moles Al from aluminium coagulants per mole P. The molar ratio of Fe : P around 3 : 1 does not exclude the possibility of $FePO_4$ precipitation as a process of phosphorus removal from wastewater coagulated with PIX, whereas the molar ratio of Al : P varying from 6 : 1 to 8 : 1 excludes the possibility of precipitation of any aluminium phosphate as a process of phosphorus removal from wastewater coagulated with aluminium coagulants. From the commercial perspective, the amount of a coagulant required to remove phosphorus from wastewater is also important. In the present study this amount remained within a relatively narrow range, ie from 4.5 mg Fe from PIX to 6.7 mg Al from $Al_2(SO_4)_3$ per mg P.

Conclusions

The model wastewater used in the study is readily treatable by chemical coagulation, which permits experimental reproducibility as well as a reliable statistical analysis of the database. The results obtained for aluminium coagulants were found to be correlated, which confirmed that the optimum dose of such coagulants can be successfully determined based on a second degree regression equation (parabola). However, the optimum dose of iron coagulants (PIX) should not be determined by this method, although it is perfectly suited for calculating the optimum dose of aluminium coagulants. PAC was the most effective of all tested coagulants, and ensured the highest level of pollutant load removal. However, this result was achieved at the highest optimum dose of this coagulant. Exceeding the optimum doses (overdosing) of all coagulants resulted in a decrease in coagulation efficiency. The negative consequences of overdosing were the least serious in the case of $Al_{2(}SO_4)_3$, and the most serious in that of PIX. The mechanism of phosphate removal may follow the Langmuir isotherm pattern, indicating a limited range of adsorption. PIX was characterized by the highest maximum adsorption capability, and adsorbed the greatest quantities of phosphates. $Al_{2(}SO_4)_3$ ensured the highest phosphorus retention levels.

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MECHANIZM USUWANIA P-PO_4 ZE ŚCIEKÓW OCZYSZCZANYCH CHEMICZNIE

Katedra Chemii, Wydział Kształtowania Środowiska i Rolnictwa,
Uniwersytet Warmińsko-Mazurski w Olsztynie

Abstrakt: Porównano zdolność koagulacyjną PAC-u, $Al_2(SO_4)_3$ i PIX-u w ściekach modelowych. Dla koagulantów glinowych potwierdzono słuszność nowej koncepcji dokładnego obliczania ilości koagulantu z warunku minimum paraboli dx = 0. Stwierdzono, że dawkę PIX-u należy obliczać ze współrzędnych przecięcia odpowiednich prostych. W warunkach „dawki optymalnej" koagulantu badano mechanizm usuwania fosforu z koagulowanych ścieków modelowych. Wartości współczynnika determinacji R^2 dla skonwertowanego równania izotermy adsorpcji Langmuira wskazały na chemiczny charakter wiązania fosforanów(V) przez koloidalne micele $\{Al(OH)_3\}$ i $\{Fe(OH)_3\}$. W konsekwencji takiej konkluzji określono stałą równowagi i „adsorpcję maksymalną" dla badanego procesu sorpcji. Ustalona molowa zależność Al:P wykluczyła chemiczne wytrącanie osadu jakiegokolwiek fosforanu(V) glinu.

Słowa kluczowe: koagulacja-flokulacja, nieorganiczne sorbenty koloidalne, ścieki modelowe, sorpcja fosforanów

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Lidia WOLNY[1], Mariusz KUGLARZ[2]
and Lucyna PRZYWARA[2]

OBSTACLES IN LIME MILK APPLICATION FOR THE TREATMENT OF FOOD INDUSTRY WASTEWATER

ZAKŁÓCENIA PROCESU OCZYSZCZANIA ŚCIEKÓW Z PRZEMYSŁU SPOŻYWCZEGO ZA POMOCĄ MLECZKA WAPIENNEGO

Abstract: It is particularly difficult to treat wastewater from the production of edible oils because of high concentration of phosphates, sulphates as well as organic compounds. What is more, the application of physicochemical methods of purification may be limited due to the varied wastewater character and its chemical properties. Phosphates precipitated by means of calcium hydroxide turn into calcium phosphates, usually in the form of hydroxyapatite (HAP), which together with an excessive amount of calcium hydroxide create well-sedimenting sludge. However, the industrial application of the method for the treatment of the analysed effluent leads to the burdensome floating sludge. The research project was carried out to establish the causes of partial sludge floating. Raw and treated wastewater (after sedimentation process) as well as sludge samples collected in the settling tank were analysed with a view to identify their chemical content. Furthermore, the sludge samples were mixed mechanically and stored in anaerobic conditions and the sedimentation process was studied in laboratory conditions. The research focused on basic physicochemical parameters, including concentration of calcium and fatty substances. It was established that the pretreatment process may be hindered by an excessive amount of fatty substances, which generate lime-fatty complex compounds. Moreover, calcium hydroxide used for phosphates precipitation lead to the release of sulphates into the treated wastewater.

Keywords: food industry wastewater, phosphates removal, coagulation, fatty substances

Food processing companies, including edible fat and oils processing companies, generate wastewater characterized by widely varied chemical composition. The wastewater composition is determined by technology used, the raw materials processed as well as applied reagents.

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[1] Institute of Environmental Engineering, Czestochowa University of Technology, ul. Brzeźnicka 60a, 42–200 Częstochowa, tel. +48 34 372 13 03, email: wolny@is.pcz.czest.pl

[2] Institute of Environmental Protection and Engineering, University of Bielsko-biała, ul. Willowa 2, Bielsko-Biała, tel. +48 33 827 91 81, email: mkuglarz@ath.bielsko.pl, l.przywara@ath.bielsko.pl

The main pollutants produced by edible fat and oils processing companies are fatty substances. Saatci [1] maintains that wastewater generated in the production of sunflower oil is polluted with linolenic acid (52.4 %), oleic acid (29.3 %) as well as arachidic acid, stearic acid and palmitic acid. Apart from fatty substances mentioned above as well as lipids, the wastewater contains total phosphorus in the range of 216–556 mg P/dm^3. The effluent is additionally polluted with substances of CODs – between 5600 and 15300 mg O_2/dm^3. The process of colza oil production also generates effluents polluted with substances of CODs – between 940 and 6364 mg O_2/dm^3; total phosphorus – between 67 and 354 mg P/dm^3, as well as sulphates – between 911 and 4210 mg SO_2/dm^3 [2].

In order to meet quality standards set by municipal sewage treatment plants and avoid high penalties, edible fat and oils companies are forced to pre-treat the wastewater they generate. Fatty substances are generally removed by means of fat traps. Whilst, phosphorus compounds are removed primarily by means of chemical precipitation. It is quite common to remove phosphates in the form of calcium phosphates at increased pH value. Orthophosphates reacting with lime milk precipitate into: amorphous tricalcium phosphatate $Ca_3(PO_4)_2$, or crystalline amorphous $Ca_5(PO_4)_3OH$, or less frequently in the form of tetracalcium phosphatate $Ca_4H(PO_4)_3$. Due to the wide range of precipitated compounds of lime and phosphorous as well as other chemical substances, it is difficult to establish exactly which chemical substances are the product of the precipitation. The types of compounds generated in the process are determined by pH, alkalinity, temperature, initial concentration of Ca/P and other substances, eg carbonates [3–5]. The lime milk added removes also sulphates, however, Ruffer [6] claims that the process of sulphates precipitation is accompanied by the generation of large amount of sludge.

Phosphates precipitated by means of calcium hydroxide in the form of hydroxy-apatite usually create well-sedimenting sludge, but the application of the method for the treatment of the examined wastewater leads to the burdensome floating sludge. Moreover, organic compounds removed become an integral part of the sludge. The main aim of the research project was to established the causes of the partial sludge floating. It was assumed that chemical reactions and biological processes might have changed the chemical composition of the sludge and caused it to float on the surface of the settling tank. In order to verify above assumptions the sedimentation process was studied in laboratory conditions.

The process of wastewater treatment

The technological process of wastewater treatment is divided into three stages: fat removal, phosphorous compounds precipitation as well as dewatering the sludge generated in the preceding stage.

Raw wastewater flows gravitally into a fat trap. The wastewater is pomped out of the last chamber of the fat trap and transferred into a reaction tank. Lime milk and flocculent, which facilitates coagulation, are dosed into that tank. Next, it is transferred into a flocculation tank, where flocs are precipitated. The wastewater leaves the flocculation tank and is directed into a settling tank. The clarified samples are neutralized to lower pH. The generated sludge is mechanically dewatered by means of a centrifuge and the sludge supernatant is recirculated into the reaction tank (Fig. 1).

Research materials and methods

The research project concerned industrial wastewater (raw and treated) as well as postsedimenting sludge from the pre-treatment plant based on phosphates precipitation by means of lime milk. Raw sewage was collected on a pipe leading to a pretreatment plant while treated sewage – directly from the settling tank. The sludge was collected from the bottom of the settling tank – referred below to as sedimenting sludge as well as from the surface of the settling tank – referred below to as floating sludge. The research materials was gathered irrespective of technological or weather conditions. Chemical analyses were carried out on the day when the samples were collected. The scope of the research project encompassed: oxidic reduction potential (ORP), pH and conductivity measurements; concentration of phosphates and sulphates; COD data; calcium ions concentration as well as fatty substances content [7]. In case of sludge, the concentration of phosphates and sulphates as well as CODs measurement was conducted in the sludge supernatant after it had been centrifuged.

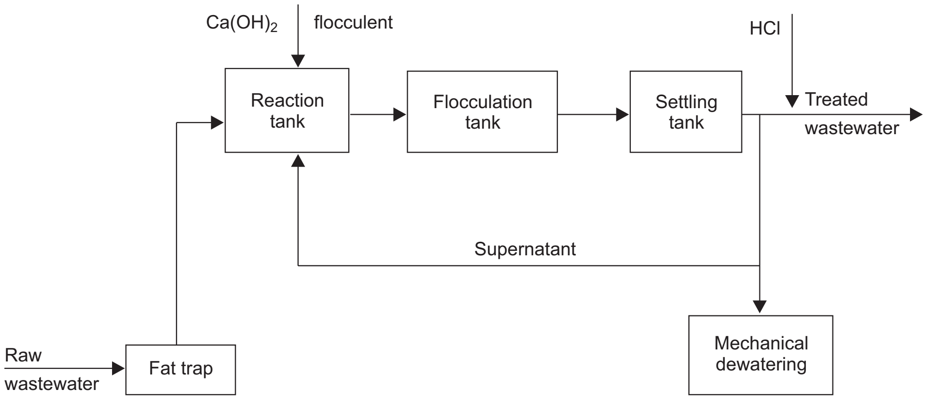

Fig. 1. The process of wastewater treatment

Discussion

The research results show that the applied method quarantees almost complete removal of phosphates – in over 90 % of cases, the average amount of phosphates does not exceed 2 mg PO_4/dm^3 (Table 1). The relatively high sulphates content in the treated wastewater proves that lime treatment is not an effective method of sulphates removal, which confirms Rüffer's explanation, according to which sulphates precipitation by means of lime reduces the content of sulphates to no less than 2000 mg SO_4/dm^3 (Table 1).

Table 1

Results of wastewater analysis

Parameter	Unit of measure	Raw sewage		Treated sewage	
		Range of variation	Average value	Range of variation	Average value
pH	—	5.66–6.05	5.95	8.95–11.05	10.32
ORP	mV	–142– –420	–203	–224– –412	–343
Conductivity	μS/cm	3550–4510	4800	5530–6360	6050
Phosphates	mg PO_4/dm^3	525–1460	1000	0.5–2.96	1.50
Sulphates	mg SO_4/dm^3	1300–3300	1430	500–2100	1890
COD	mg O_2/dm^3	2200–8500	5000	500–3100	1800
Ether extract	g/dm^3	1.20–3.30	2.18	0.04–0.12	0.07

What is more, the lime treatment reduces the amount of CODs by about 60 %. Since fatty substances might have been retained in sludge, the level of fats measured as a ether extract in both raw and treated samples was monitored. It was also confirmed that applied method removes over 95 % of fatty substances (Table 1).

Next, sedimenting and floating sludge were investigated. The sedimenting sludge exhibited ORP at the level of between –210 and –500 mV, while the floating sludge showed ORP at the level of between od –390 do – 450 mV. In case of the floating sludge, a narrow ORP range allows to conclude that the processes involved are exclusively anaerobic in nature. It was also established that there are significant differences between these sludges in terms of conductivity – the supernatant of the floating sludge exhibited conductivity which was higher by about 1000 μS/cm – on average. The difference may be caused by low content of sulphates in the floating sludge.

The average level of sulphates in the floating sludge at 350 mg SO_4/dm^3 was rather unexpected. It cannot be convincingly explained because the raw wastewater, treated wastewater as well as sedimenting sludge contained almost the same amount of sulphates. Taking into account strongly reductive and thus anaerobic conditions, it is assumed that sulphates can be only converted into sulphides and hydrogen sulfide.

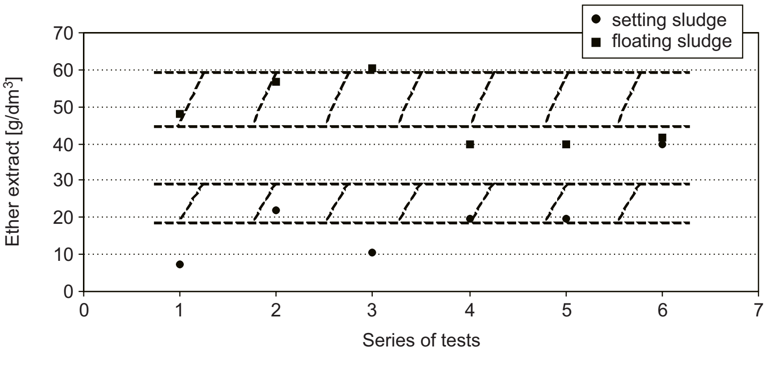

Fig. 2. Fatty substances content – measured as an ether extract

The removal of CODs and fatty substances from the wastewater by means of lime treatment, influences the chemical composition of the sludge. The sedimenting sludge contains between 10 and 20 g/dm^3 of fatty substances, while the floating sludge contains at least three times as much of these compounds– between 40 and 60 g/dm^3 (Fig. 2).

Figure 3 presents the amount of fatty substances in sludge samples – expressed in a different way, ie as a percentage of sludge solids.

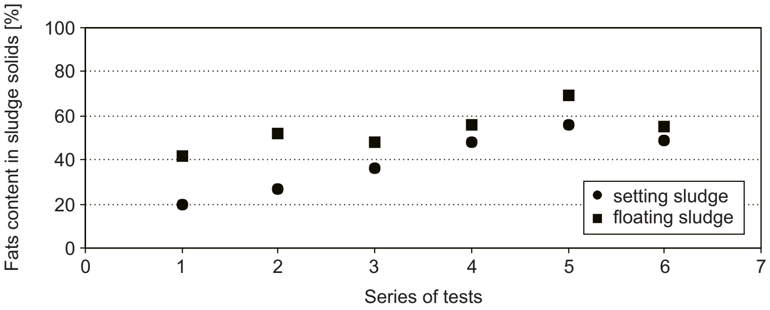

Fig. 3. Percentage of fatty substances in the sludge solids

The amount of calcium ions in the floating sludge fluctuated between 2000 mg Ca^{2+}/dm^3 and 3125 mg Ca^{2+}/dm^3, whereas in the sedimenting sludge – between 937 mg Ca^{2+}/dm^3 and 2681 mg Ca^{2+}/dm^3. The research results presented above allow to conclude that greater amount of calcium ions in sludge is connected with the higher content of fatty substances.

As mentioned above, with a view to investigate the processes in the settling tank, sludge samples were stored in laboratory conditions. It was proved in a series of tests that the pH value decreased slightly and the conductivity value increased. The latter may be associated with an increase in sulphates concentration. Figure 4 presents changes in sulphates concentration in several selected series of tests.

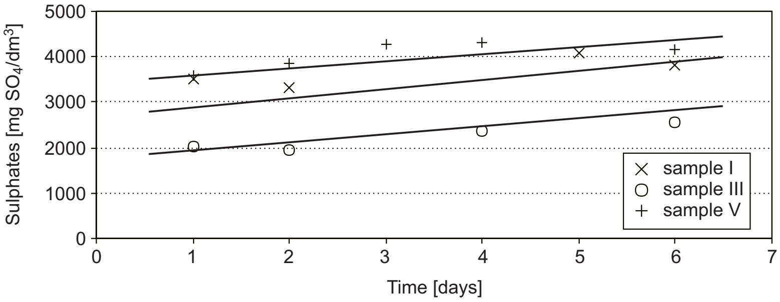

Fig. 4. Changes in sulphates concentration (in selected series of tests)

Moreover, the concentration of CODs increased significantly – Figure 5. It is likely that fatty substances are decomposed in anaerobic conditions into easier oxidating compounds which are also counted as CODs, eg fatty acids.

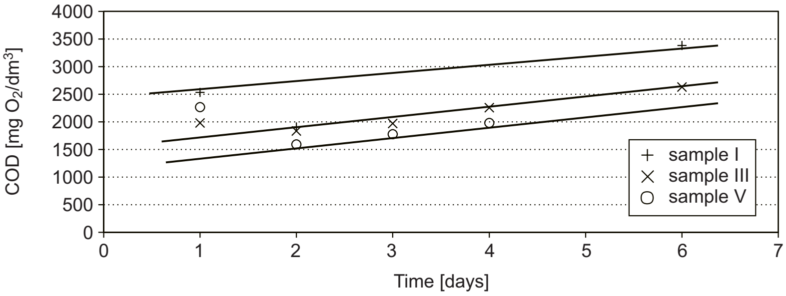

Fig. 5. Changes in CODs concentration (in selected series of tests)

The level of calcium ions recorded throughout the experiment basically does not allow to draw any conclusion as to the character of chemical processes in the sludge. It may only be mentioned that in most cases the level of calcium ions increased in the sludge and decreased in the supernatant phase.

Conclusions

The aim of the research project was to establish the origin of burdensome surface sludge which interferes with the process of chemical pre-treatment. The floating sludge is a side effect of wastewater being treated with lime milk which is used to precipitate phosphates. It is highly probable that flotation may be caused by an increased level of fatty substances in the sludge from the settling tank, which was confirmed by the results of conducted chemical analyses. What is more, greater level of fatty substances in the sludge is connected with higher content of calcium ions. Due to coagulative properties, lime can generate compounds with fatty substances, which may be further modified and deposited on the surface of the sludge.

Moreover, with the view to investigate the technological process, the sludge was stored and mixed mechanically in laboratory conditions. The research results confirmed that the sludge changed its physicochemical properties in the following way: pH value decreased slightly; conductivity value increased; concentration of sulphates increased – it is highly probable that sulphates ions are released from precipitated calcium sulphates. What is more, released sulphates also disrupt the process. It has also been proved that CODs increased throughout the experiment – it may caused by decomposing in anaerobic conditions into easier oxidating compounds which are also measured as CODs. The latter also include fatty substances.

Acknowlegments

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ZAKŁÓCENIA PROCESU OCZYSZCZANIA ŚCIEKÓW Z PRZEMYSŁU SPOŻYWCZEGO ZA POMOCĄ MLECZKA WAPIENNEGO

Instytut Inżynierii Środowiska, Politechnika Częstochowska
Instytut Ochrony i Inżynierii Środowiska, Akademia Techniczno-Humanistyczna

Abstrakt: Ścieki pochodzące z produkcji olejów jadalnych są trudne do oczyszczenia ze względu na duże stężenia fosforanów, siarczanów i związków organicznych. Ze względu na zróżnicowany charakter i skład ścieków przemysłowych stosowanie fizykochemicznych metod usuwania zanieczyszczeń może być związane z pewnymi ograniczeniami. Podczas strącania fosforanów za pomocą wapna powstają fosforany wapnia zazwyczaj w postaci hydroksyapatytu (HAP), który wraz z nadmiarem wodorotlenku wapnia tworzy dobrze sedymentujący osad. Zastosowanie tej metody do oczyszczania badanych ścieków w warunkach technicznych powoduje powstawanie uciążliwego osadu flotującego na powierzchni ścieków. Szukając przyczyn wypływania części osadów, wykonano badania obejmujące charakterystykę jakościową ścieków dopływających oraz po procesie sedymentacji, a także osadów zatrzymywanych w osadniku. Zmierzając do lepszego poznania procesów zachodzących w osadniku, badano wpływ mieszania mechanicznego na osady przetrzymywane w warunkach laboratoryjnych. Analizowano podstawowe parametry fizykochemiczne, w tym zawartość wapna oraz substancji tłuszczowej. Stwierdzono, że obecność w ściekach tłuszczy w znacznych stężeniach przyczynia się do powstawania związków wapniowo-tłuszczowych flotujących na powierzchni ścieków, co w rezultacie zakłóca proces podczyszczania ścieków. Ponadto wapno stosowane do strącania fosforanów przyczynia się do uwalniania jonów siarczanowych.

Słowa kluczowe: ścieki przemysłowe, usuwanie związków fosforu, koagulacja, substancje tłuszczowe

Varia

INVITATION FOR ECOPOLE '09 CONFERENCE

CHEMICAL SUBSTANCES IN ENVIRONMENT

We have the honour to invite you to take part in the 18th annual Central European Conference ECOpole '09, which will be held in **14–17 X 2009** (Thursday–Saturday) on Wilhelms Hill at Uroczysko in Piechowice, PL.

The Conference Programme includes oral presentations and posters and will be divided into four sections – SI, SII, SIII and SIV:

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

On the first day the debates of sections SI and SII will take place. The second day will be started with an ecological excursion. Afterwards the plenary Session with lectures on **environmental education** as well as **grants within the EU Programmes** and presentation of **EU Centres of Excellence** will be held. Then the **Forum of Young Scientists** – the presentation (lectures and posters) of young scientists work will take place.

The main topic of the third day is the influence of environment quality on the **human health**.

During the Conference an exhibition of publications concerned with conference topics will be also organised.

The Conference language is English.

Contributions to the Conference will be published as:

- abstracts on the CD-ROM (0.5 page of A4 paper sheet format)
- extended abstracts (4–6 pages) in the semi-annual *Proceedings of ECOpole*;

full papers will be published in successive issues of the *Ecological Chemistry and Engineering/Chemia i Inżynieria Ekologiczna* (Ecol. Chem. Eng.).

Additional information one could find on the Conference website:

ecopole.uni.opole.pl

The deadline for sending the Abstracts is **15.07.2009** and for the Extended Abstracts: **1.10.2009**. The actualised list (and the Abstracts) of the Conference contributions accepted for presentation by the Scientific Board, one will find (starting from 15.07.2009) on the Conference website.

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

The Conference fee is 300 € (covering hotel, meals and transportation during the Conference). It could be reduced (to 170 €) for young people actively participating in the Forum of Young Scientists. But the colleague has to deliver earlier the Extended Abstract (4-6 pages) of his/her contribution (deadline is on 15.08.2009), and a recommendation of his/her Professor.

Fees transferred after 15.09.2009 are 10% higher.

At the Reception Desk each participant will obtain a CD-ROM with abstracts of the Conference contributions as well as Conference Programme (the Programme will be also published on the Conference website).

Further information is available from:
Dr hab. Maria Wacławek, prof. UO
Chairperson of the Organising Committee
of ECOpole '09 Conference
University of Opole
email: Maria.Waclawek@uni.opole.pl
and mrajfur@o2.pl
tel. +48 77 455 91 49 and +48 77 401 60 42
fax +48 77 401 60 51

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REGISTRATION FORM FOR THE ECOpole ’09 CONFERENCE

Surname and First Name . . . .

Scientific Title/Position . . . .

Affiliation . . . .

Address . . . .

Tel./fax . . . . email . . . .

Title of presentation . . . .

. . . .

KIND OF PRESENTATION

	YES	NO
Oral		
Poster		
Taking part in discussion		

ACCOMMODATION

14/15 X		15/16 X		16/17 X	
YES	NO	YES	NO	YES	NO

MEALS

Date	Breakfast	Lunch	Dinner
14 X	—	—	
15 X			
16 X			
17 X			—

✂ -

ZAPRASZAMY
DO UDZIAŁU W ŚRODKOWOEUROPEJSKIEJ KONFERENCJI
ECOpole ’09
w dniach 14–17 X 2009

SUBSTANCJE CHEMICZNE W ŚRODOWISKU PRZYRODNICZYM

Będzie to osiemnasta z rzędu konferencja poświęcona badaniom podstawowym oraz działaniom praktycznym dotycząca różnych aspektów ochrony środowiska przyrodniczego. Odbędzie się ona w ośrodku „Uroczysko” na Wzgórzu Wilhelma w Piechowicach. Doroczne konferencje ECOpole mają charakter międzynarodowy i za takie są uznane przez Ministerstwo Nauki i Szkolnictwa Wyższego. Obrady konferencji ECOpole ’09 będą zgrupowane w czterech Sekcjach SI–SIV:

Obrady konferencji ECOpole ’08 będą zgrupowane w czterech Sekcjach SI–SIV:

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

Materiały konferencyjne będą opublikowane w postaci:

- abstraktów (0,5 strony formatu A4) na CD-ROM-ie;
- rozszerzonych streszczeń o objętości 4-6 stron w półroczniku *Proceedings of ECOpole*;
- artykułów: w abstraktowanych czasopismach: *Ecological Chemistry and Engineering/Chemia i Inżynieria Ekologiczna* (*Ecol. Chem. Eng.*) oraz niektórych w półroczniku *Chemia – Dydaktyka – Ekologia – Metrologia*.

Termin nadsyłania angielskiego i polskiego streszczenia o objętości 0,5–1,0 strony (wersja cyfrowa + wydruk) planowanych wystąpień upływa w dniu 15 lipca 2009 r. Lista prac zakwalifikowanych przez Radę Naukową Konferencji do prezentacji będzie sukcesywnie publikowana od 15 lipca 2009 r. na stronie webowej konferencji

ecopole.uni.opole.pl

Aby praca (dotyczy to także streszczenia, które powinno mieć tytuł w języku polskim i angielskim, słowa kluczowe w obydwu językach) przedstawiona w czasie konferencji mogła być opublikowana, jej tekst winien być przygotowany zgodnie z wymaganiami stawianymi artykułom drukowanym w czasopiśmie *Ecological Chemistry and Engineering*, które jest dostępne w wielu bibliotekach naukowych w Polsce i zagranicą. Są one takie same dla prac drukowanych w półroczniku *Chemia – Dydaktyka – Ekologia – Metrologia*. Zalecenia te są również umieszczone na stronie webowej konferencji.

Koszt uczestnictwa w całej konferencji wynosi 1000 zł i pokrywa opłatę za udział, koszt noclegów i wyżywienia oraz rocznej prenumeraty Ecol. Chem. Eng. (razem blisko 2000 ss.) łącznie z materiałami Konferencji. Jest możliwość udziału tylko w jednym wybranym przez siebie dniu, wówczas opłata wyniesie 650 zł i będzie upoważniała do uzyskania wszystkich materiałów konferencyjnych, jednego noclegu i trzech posiłków (śniadanie, obiad, kolacja), natomiast osoby zainteresowane udziałem w dwóch dniach, tj. w pierwszym i drugim lub drugim i trzecim, winny wnieść opłatę w wysokości 800 zł. Opłata dla magistrantów i doktorantów oraz młodych doktorów biorących aktywny udział w Forum Młodych może być zmniejszona do 600 zł, przy zachowaniu takich samych świadczeń. Osoby te winny dodatkowo dostarczyć: rozszerzone streszczenia (4–6 stron) swoich wystąpień (**do 15.08.2009 r.**). Jest także wymagana opinia opiekuna naukowego. Sprawy te będą rozpatrywane indywidualnie przez Radę Naukową oraz Komitet Organizacyjny Konferencji. Członkowie Towarzystwa Chemii i Inżynierii Ekologicznej i Polskiego Towarzystwa Chemicznego (z opłaconymi na bieżąco składkami) mają prawo do obniżonej opłaty konferencyjnej o 25 zł. Opłaty wnoszone po dniu 15 września 2009 r. są większe o 10% od kwot podanych powyżej. Wszystkie wpłaty winne być dokonane na konto w Banku Śląskim:

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i mieć dopisek ECOpole ’09 oraz nazwisko uczestnika konferencji.

Po konferencji zostaną wydane 4–6-stronicowe rozszerzone streszczenia wystąpień w półroczniku *Proceedings of ECOpole*. Artykuły te winny być przesłane do **1 października 2009 r**. Wszystkie nadsyłane prace podlegają zwykłej procedurze recenzyjnej. Wszystkie streszczenia oraz program Konferencji zostaną wydane na CD-ROM-ie, który otrzyma każdy z uczestników podczas rejestracji. Program będzie także umieszczony na stronie webowej konferencji.

Za Komitet Organizacyjny
dr hab. inż. Maria Wacławek, prof. UO
Wszelkie uwagi i zapytania można kierować na adres:
Maria.Waclawek@uni.opole.pl
lub mrajfur@o2.pl
tel. 077 401 60 42
tel. 077 455 91 49
fax 077 401 60 51

Kalendarium

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ZGŁASZAM UCZESTNICTWO W KONFERENCJI ECOpole ’09
(Prosimy o wypełnienie zgłoszenia drukowanymi literami)

Nazwisko i imię . . . .

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Miejsce pracy . . . .

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Dane instytucji (nazwa, adres, NIP), dla której ma być wystawiona faktura: . . . .

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RODZAJ PRZEWIDYWANEGO WYSTĄPIENIA:

	TAK	NIE
Referat		
Poster		
Głos w dyskusji		

TYTUŁ WYSTĄPIENIA . . . .

. . . .

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14/15 X		15/16 X		16/17 X	
TAK	NIE	TAK	NIE	TAK	NIE

ZAMAWIAM POSIŁKI

Data	Śniadanie	Obiad	Kolacja
14 X	—	—	
15 X			
16 X			
17 X			—

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GUIDE FOR AUTHORS
ON SUBMISSION OF MANUSCRIPTS

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Professor Witold Wacławek
Editorial Office of monthly *Ecological Chemistry and Engineering*
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Uniwersytet Opolski
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Tel. +48 77 452 71 34, fax +48 77 455 91 49,
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Papers submitted are supposed to be written in English language and should include a summary and keywords, if possible also in Polish language. If not then the Polish summary and keywords will be provided by the Editorial Office. All authors are requested to inform of their current addresses, phone and fax numbers and their email addresses.

It is urged to follow the units recommended by the *Systéme Internationale d'Unites* (SI). Graph axis labels and table captions must include the quantity units. The use of the following commonly applied expressions is recommended: mass – m/kg, time – t/s or t/min, current intensity – I/A; thermodynamic temperature – T/K, Celsius scale temperature – t/°C or θ/°C (if both time and Celsius scale units need to be used, the symbol θ/°C for temperature is to be taken) etc.

Symbols recommended by the International Union of Pure and Applied Chemistry (Pure and Appl. Chem., 1979, **51**, 1–41) are to be followed.

Graphics (drawings, plots) should also be supplied in the form of digital vector – type files, *e.g.* Corel-Draw, Grapher for Windows or at least in a bitmap format (TIF, PCK, BMP). In the case of any query please feel free to contact with the Editorial Office.

Footnotes, tables and graphs should be prepared as separate files.

References cited chronologically should follow the examples given below:

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[2] Nowak S: Chemia nieorganiczna, WNT, Warszawa 1990.

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Przypisy i tabele podobnie jak rysunki zapisujemy jako osobne pliki.

Literaturę prosimy zamieszczać wg poniższych przykładów:

[1] Kowalski J. and Malinowski A.: Polish J. Chem. 1990, **40**, 2080–2085.

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