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The role of commodity science in quality management in a knowledge-based economy

Ecological and environmental aspects of commodity science as a quality science

Ekologiczne i środowiskowe aspekty towaroznawstwa jako nauki o jakości

Red. Joanna Newerli-Guz

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pod redakcją Joanny Newerli-Guz

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SPIS TREŚCI

GROWING OF FILAMENTOUS FUNGI ON BACTERIAL CELLULOSE FILM CONTAINING MINT EXTRACTS

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Abstract
A bacterial cellulose film was prepared, which was then modified with the addition of extracts of mint. The obtained film was treated with filamentous fungi in order to check the degree of fouling of the cellulose surface by fungi. Despite the fact that the fungicidal properties of the extracts used were not found, the phenomena of sporulation decay and the degradation of the hyphae in the place of their occurrence were observed during the research.

Keywords: bacterial cellulose film. *Mentha spp*., filamentous fungi

1. Introduction

Cellulose is a natural plant product, which is a structural component of cells and gives tissues tensile strength.For industrial purposes, most cellulose is obtained from wood. The demand for industrial pulp is huge and is constantly growing.It is estimated that by 2024 the demand will be approximately 77.7 million tonnes [https://www.researchandmarkets.com]. Cellulose is a material commonly used in many industries.Its resources are consumed by the paper and packaging industry. It is also used in cosmetology, pharmacy, chemical and textile industries. Extracting cellulose from plant tissue contributes to the partial deformation of the polymer, e.g.reducing the degree of polymerization, which negatively affects its physical and mechanical properties. Separating cellulose from lignin and hemicellulose requires an additional investment of a huge amount of chemicals based on sulfur, nitrogen and chlorine compounds, which are not neutral to the environment. According to Ali and Sreekrishnan [2001], the processing of plant cellulose releases significant amounts of greenhouse gases into the environment, and the pulp and paper industry is in the sixth place in the world in terms of pollutant emissions to the environment.

It seems that a good alternative to plant cellulose may be its microbiological counterpart, the so-calledbacterial cellulose.The ability to synthesize bacterial cellulose is demonstrated by many microorganisms, although the *Komogataeibacter xlinus* bacterium dominates the synthesis. Bacterial cellulose, in contrast to its plant counterpart, is characterized by a higher degree of polymerization [Betlej et al. 2022], crystallinity [Czaja et al. 2004] as well as the size of the fibers and their spatial arrangement [Stanisławska 2016]. These unique features give bacterial cellulose a greater tensile strength, as well as different water absorption and hygroscopicity than in the case of plant cellulose. Another positive feature of bacterial cellulose is the lack of additional components that are difficult to separate, such as in the case of wood, e.g. lignin.Chemically pure bacterial cellulose is non-toxic, completely biodegradable and biocompatible, which makes it suitable for the production of medical devices as a dressing material [Ullah et al. 2016].The mentioned properties of cellulose enable the bacterial polymer to successfully substitute plant cellulose.

The biggest obstacle for the industrial use of bacterial cellulose is the still high cost of its synthesis and the insufficient scale of production. The cost of microbiological media for the cultivation of cellulose-synthesizing microorganisms accounts for 30 % of the total production costs [Rivas et al. 2004], due to which the scale of its production is still at a low level. Finding cost-effective and low-cost methods of polymer synthesis will allow for its widespread use for application purposes.

The potential uses of bacterial cellulose are enormous. The use of bacterial cellulose in the pulp and paper and packaging industries may be of particular importance.

Even a relatively small addition of bacterial cellulose to the recycled pulp can improve the properties of recycled paper [Gallegos et al. 2016], and its share in the production of packaging materials increases their biodegradability [Qasim et al. 2021]. Bacterial cellulose, which can be easily chemically modified due to the presence of numerous hydroxyl groups, enables its use in the production of antibacterial films [Yin et al. 2020] or impermeable packaging for liquids and gases [Bednarczyk et al. 2021]. Modifications of bacterial cellulose can be carried out at the stage of cultivation by introducing into the microbial medium substances that are incorporated into the polymer structure [Chen et al. 2009]. Albuquerque et al. [2020] showed that the addition of clove oil to bacterial cellulose not only reduces the growth of microorganisms on the polymer surface by 65%, but also improves the mechanical and thermal properties. In turn, in the studies conducted by Zhou et al. [2022] It has been shown that the addition of cinnamon oil to the bacterial cellulose-natural curdlan complex improves its barrier properties.

One of the challenges in the area of improving the properties of biomaterials based on bacterial cellulose is to strengthen its immediate resistance to the action of microorganisms, therefore the aim of this study was to determine whether the addition of an water extract of various species and cultivars of mint to the mass of the ground bacterial cellulose used to form the film affects on the growth dynamics of cellulose-decomposing fungi on the film.

2. Material and methods

Bacterial cellulose was obtained in the process of microbiological cultivation of a consortium of bacteria and yeasts known as SCOBY. The microorganisms were grown on a liquid medium containing 10% food sucrose and 0.03% peptone. The cultivation was carried out for 21 days in a heat incubator under the conditions of temperature and relative air humidity of 26 ± 2 °C and 66 ± 2%, respectively. After the completion of the culture stage, cellulose was removed from the surface of the culture, and then it was cleaned of the residues of microorganisms and the post-culture medium by rinsing in distilled water and NaOH. The purification process of bacterial cellulose was carried out by washing twice in distilled water, then rinsing in 0.1 M NaOH at 90 °C for 30 minutes, rinsing again in distilled water, and then in 0.1% citric acid to adjust the pH to neutral. After the end of the purification process, the polymer was washed twice more in distilled water and left in a refrigerator at 4 °C until processing.

The mint used to prepare the water extracts came from experimental crops in the fields of the Center for Research and Scientific Innovation in Wola Zadybska near Lublin (Poland) (51°44’49”N21°50’38”E). Mints were grown in loess loam soil. Cultivation and harvest were carried out in 2020. All the mints used in the studies were grown under the same conditions. The mints were harvested in June 2020, when the plants were in a fully developed vegetative phase, fully branching, with fully developed shoots, but before the formation of flower buds. The plants were cut at a height of about 10 cm above the ground, and then immediately dried by convection in a laboratory drier with forced air circulation at 32 ºC. After drying, the leaves were separated from the stems. The mint leaves were used to prepare water extracts.

The mints used in the research belonged to 4 cultivars (*M. spicata* ‘Morocco’ - M3, *M. spicata* ‘Crispa’ - M5, *M. × piperita* ‘Almira’ - M6, *M. suaveolens* ‘Variegata’ - M8).The leaves of these mints contained essential oil of various compositions. The composition of the dominant oils in the used mints was determined by Ludwiczuk et al. [2016]:

M. spicata ‘Morocco’ – carvone and *cis*-dihydrocarvone

M. spicata ‘Crispa’ – carvone

M. × piperita ‘Almira’ – piperitenone oxide and piperitenone

M. suaveolens ‘Variegata’ – piperitenone

In order to prepare water extracts, 10 g of mint leaves were weighed and 200 ml of hot water at 100 °C were poured over them. The infusions prepared in this way were placed on a shaker.The shaking time was 24 h and the rotation speed was between 100-120 rpm. After this time, the leaves were separated from the extract, and the extract was filtered through a syringe filter with a pore diameter of 0.22 μm in order to remove contaminants, including potential microbiological contamination.

2.1 Preparation of bacterial cellulos film with the addition of mint extract

Bacterial cellulose was pre-crushed using a laboratory grinder and then homogenized to the form of particles.The cellulose homogenate was divided into appropriate portions to which various amounts of water extracts of mint were added (Table 1):

Table 1. Materials used in the research

No.	Bacterial cellulose (g)	Mint extract (ml)	
Ch_M3_15 Tv_M3_15	*85*	*15*	*M. spicata 'Morocco'*
Ch_M3_25 Tv_M3_25	*65*	*25*	
Ch_M5_15 Tv_M5_15	*85*	*15*	*M. spicata 'Crispa'*
Ch_M5_25 Tv_M5_25	*65*	*25*	
Ch_M6_15 Tv_M6_15	*85*	*15*	*M. × piperita 'Almira'*
Ch_M6_25 Tv_M6_25	*65*	*25*	
Ch_M8_15 Tv_M8_15	*85*	*15*	*M. suaveolens 'Variegata'*
Ch_M8_25 Tv_M8_25	*65*	*25*	
Ch_K Tv_K	*100*	-	

Ch – Ch. globosum, Tv- T. versicolor, M3, 5, 6, 8 – number of Mentha spp., 15, 52 – mint extract dose, K- control

Source: own study.

The crushed bacterial cellulose with the addition of water extracts was thoroughly mixed using a blender, and then placed and spread on a silicone mold.The cellulose prepared in this way was dried in a laboratory dryer until constant weight was obtained. Forms with a diameter of 30 mm were cut out of the films prepared in this way and sterilized in UV rays for 30 minutes.

2.2 Assessment of the degree of fouling of cellulose films by fungi

The degree of fouling of cellulose films by mold fungi was assessed on the maltose-agar medium. The microbiological medium containing 2.5% maltose extract and 2.5% agar was poured in an amount of 10 ml into petri dishes with a diameter of 90 mm.Plastic spacers were placed centrally on the substrate to separate the cellulose from the surface of the medium. The mold fungus inoculum of *Trichoderma viride* Pers., Strain A-102 and *Chaetomium globosum* Kunze strain A-141 (ATCC 6205), approximately 3 mm in size, was inoculated on the medium at four equal intervals around the cellulose samples. The degree of growth of cellulose samples by fungi was determined on the basis of high-resolution photographic photos (on a laboratory stand for taking photos for documentation purposes) taken periodically for each tested sample. The growth of fungi on the sample was determined as the percentage of the growth of the sample by the mycelium in relation to the total area of the test sample. The percentage of coverage with an accuracy of 5% was determined with ImageJ2 image analysis software (Fiji v.1.52i) [Borysiuk et al. 2022]. Each study was performed in 4 replications. Control samples did not contain the addition of mint extract.

3. Results

The results of the research indicate that the water mint extracts added to bacterial cellulose do not adversely affect the growth dynamics of *Ch. globosum* and *T. viride*, which degrade cellulose. Additionally, it can be seen that the addition of larger amounts of mint extracts stimulates the growth of fungi on the cellulose film (Figure 2, 4). Only in the case of the cellulose film containing the addition of *M.* × *piperita* ‘Almira’ mint extract in the amount of 25 ml/65 g of cellulose homogenate, less intensive growth of *Ch. globosum* was observed compared to the control sample and cellulose tests containing extracts of *M. spicata* ‘Morocco’, *M. spicata* ‘Crispa’ and *M. suaveolens* ‘Variegata’. Interesting observations were also made of the growth dynamics of *T. viride* on cellulose with the addition of higher concentrations of *M.* × *piperita* 'Almira' (Figure 4).In the last days of growth measurement, a clear disappearance of sporulation and degradation of hyphae were observed in the place where the fungal colony was spreading on the sixth day of cultivation (Figure 5). The observed phenomenon will require more careful study in the future. The lower proportion of mint extract in bacterial cellulose slowed down the growth dynamics of the tested fungi, especially in the last day of the measurement (Figure 1, 3). Mint extract *M.* × *piperita* 'Almira' had the greatest impact on the growth dynamics of the studied fungi.

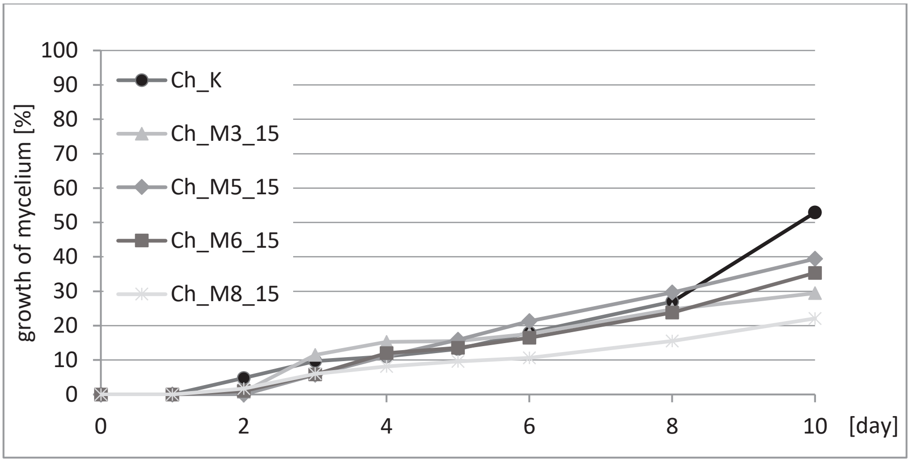

Fig. 1. Growth dynamics of *Ch. globosum* on the surface of bacterial cellulose film with a smaller share of mint extract

Source: own study.

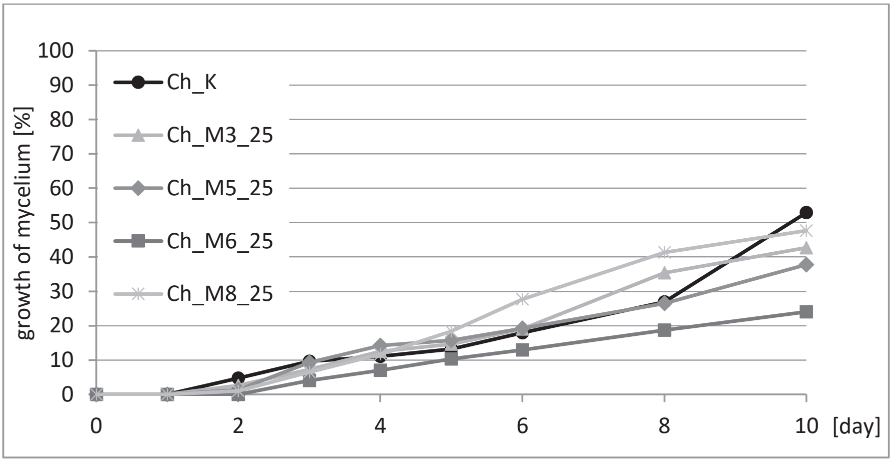

Fig. 2. Growth dynamics of *Ch. globosum* on the surface of bacterial cellulose film with a greater share of mint extract

Source: own study.

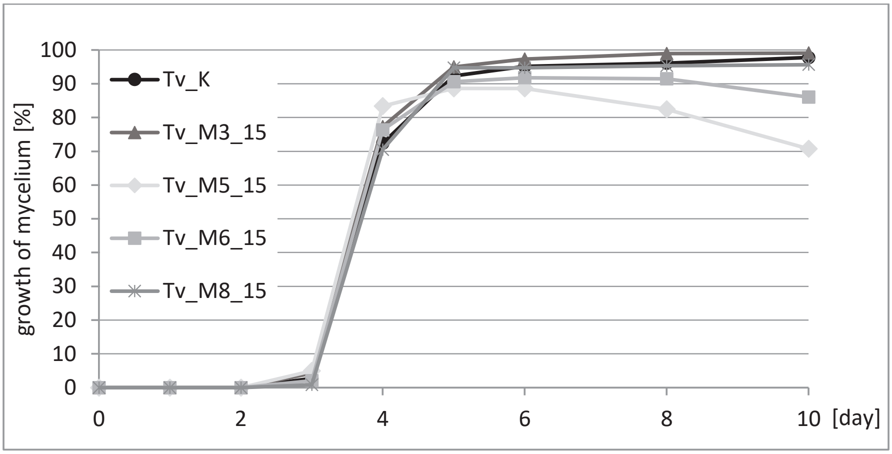

Fig. 3. Growth dynamics of *T. viride* on the surface of bacterial cellulose film with a smaller share of mint extract

Source: own study.

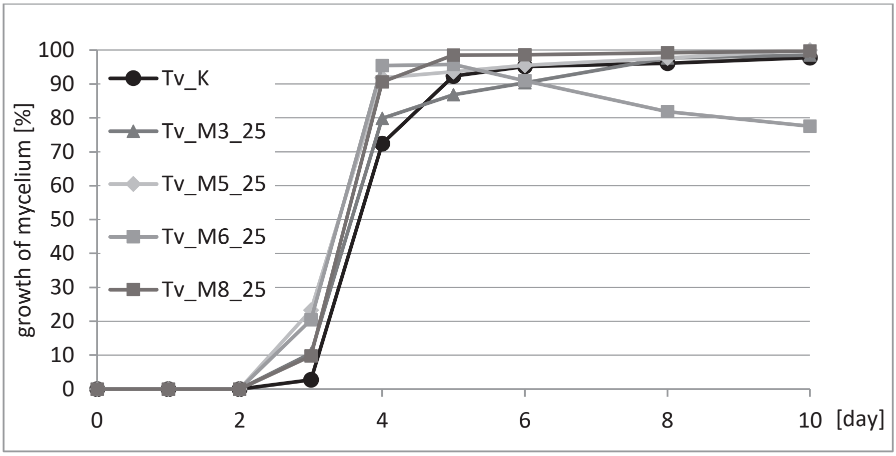

Fig. 4. Growth dynamics of *T. viride* on the surface of bacterial cellulose film with a greater share of mint extract

Source: own study.

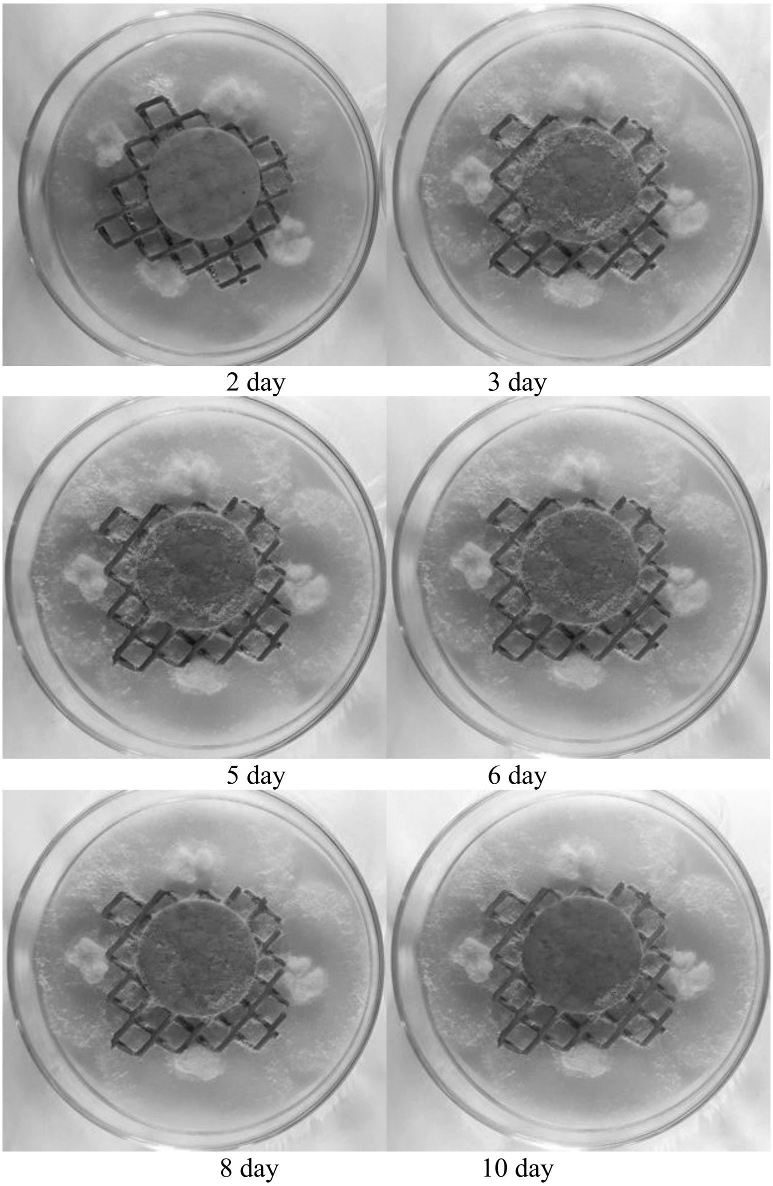

Fig. 5. Visualization of *T. viride* growth changes on bacterial cellulose containing the *M. × piperita* 'Almira' extract

Source: own study.

4. Discussion

Mint leaves are rich in chemicals with antimicrobial properties. Phenolic compounds and terpenoids contained in essential oils show bactericidal and fungicidal properties. The mints used, according to those described by Ludwiczuk et al. [2016] research results are rich in compounds such as piperitenone and carvone. Although the obtained results do not prove the inhibitory effect of the used mint extracts against cellulose-decomposing fungi, they indicate that the presence of the extracts in the substrate, which is bacterial cellulose, affects the morphological features of the fungi. Evidence of this effect is the disappearance of sporulation and the degradation of the hyphae of *T. viride* in the final stages of the observations. Research by Jurić et al. [2021] prove that natural mint extracts have antibacterial activity against *Staphylococcus aureus, Escherichia coli, Salmonella enterica* and *Pseudomonas aeruginosa*. On the other hand, in studies conducted by Abd El-Aziz et al. [2018] the fungicidal effect of mint extract added to chitosan nanoparticles was proven.Interesting studies of the fungicidal properties of various *Mentha longifolia* extracts were carried out by Yazgi et al.[2015]. The authors of the research showed that not only the type of solvent used for the extraction, but also the morphological parts of the plant used as the starting material determine the fungicidal properties of the mint used.

Natural substances can be successfully used as an ingredient of packaging with antimicrobial properties.The durability of food by increasing its shelf-life is a key task of the United Nations aimed at reducing global food waste per capita. Therefore, it seems that the introduction of active polymers containing fungicides or antibacterial ingredients to the market is a solution that not only enables the development of new technologies, but also a solution that will contribute to reducing the loss of goods in production and supply chains. Additionally, it can be noticed that against the background of the effects of the COVID-19 pandemic, not only the consumer awareness of hygiene has increased, but also the acceptance of the need for new preparations and technologies as methods of preventing the spread of microorganisms. Therefore, it can be concluded that the development of research on active materials with aseptic properties will contribute to the scaling of the innovation market.

5. Conclusions

The obtained results concerning the modification of bacterial cellulose by mint extracts indicate that the applied water mint extracts do not show fungicidal properties, but have an impact on the dynamics of fungus growth, which was observed in the case of films with a lower share of mint extract. Additionally, the research showed the phenomenon of the disappearance of sporulation and hyphae at the site of the fungus on the surface of the cellulose.this phenomenon certainly requires a deeper analysis and additional research.

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PHOSPHATE IN SEWAGE – MODELLING, IDENTIFICATION AND PREDICTION

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Abstract
The paper is devoted presentation the probabilistic model of the process of phosphate concentration changes in sewage collected in the exemplary wastewater treatment plant. The proposed process is described by defining its basic notions such as the states of phosphate concentration in sewage and next methods and procedures of estimating its unknown parameters are used to determine them. The methods of the process of phosphate concentration changes in sewage identification and prediction are presented and used to obtain the following final results: approximate limit values of transient probabilities and the approximate mean values of sojourn total time of the fixed time interval at the particular states of the process.

Keywords: sewage, wastewater treatment plant, nutrients, semi-Markov process

Introduction

The phenomenon defined as the increase in concentration of plant nutrients e.g. phosphorus and nitrogen in an aquatic ecosystem such as lake or sea is defined as an eutrophication. The productivity such an ecosystem increases simultaneously with the amount of organic material that can be broken down into nutrients increases. The large inputs of nutrients coming from debris, products of the reproduction and death terrestrial organisms, enter the ecosystem primarily by runoff from land. The agriculture and wastewaters are usually the major anthropogenic source of nutrients.

Therefore the elimination of nutrients from sewage is one of the goals of wastewater treatment plants as these ones cause the eutrophication when entering seawater. The intensive and anthropogenic eutrophication is a negative phenomenon, causing the large algae and other microscopic organisms blooms, oxygen depletion as well as the aesthetic nuisance of sea recreation areas and other undesirable effects.

Wastewater treatment in a biological wastewater treatment plant (WWTP) is a complex process combining physical, chemical and biological processes. Changes in wastewater flow rate and composition, combined with time-varying reactions in the biomass of the activated sludge, make the process nonlinear and unsteady. The efficiency of the purification process is determined by measuring quantities indicative of the quality of the treated wastewater, which, however, can only be determined after the process is completed. Since there is no way to undo the stages of the process, all errors in process control can cause small- or large-scale violations of the ecosystem. Therefore, mathematical models that adequately describe the process can be the basis for monitoring and optimal control of WWTPs (Serdarevic & Dzubur 2016). It has become particularly useful for meet effluent limits for nitrogen and phosphorus removal. Modelling and understanding the process of phosphorus removal is of key importance, as phosphorus contributes to eutrophication effects if led directly out to surrounding surface waters. Phosphorus removal processes strictly depend on the composition of wastewater, and in particular on the concentration of dissolved forms of phosphorus (PO_4-P). This value can fluctuate significantly in wastewater flowing into WWTP. The purpose of this study is to develop a probabilistic model of the process of changes in phosphate concentration in inflow of an exemplary biological wastewater treatment plant.

1. Material and methods

1.1. Modelling process of phosphate concentration in wastewater

The process of phosphate (PO_4-P) concentration in wastewater $\Phi(t)$, $t \in \langle 0,+\infty)$ with the states of phosphate concentration in wastewater from the set $\{\varphi_1, \varphi_2,..., \varphi_v\}$ is defined. It is assumed that the phosphate concentration in wastewater takes v, $v \in N$ different concentration states $\varphi_1, \varphi_2,..., \varphi_v$, that have an influence on quality of wastewater. Next, a semi-Markov model of the process of PO_4-P concentration in wastewater $\Phi(t)$, $t \in \langle 0,+\infty)$ is assumed. Its random conditional sojourn time at the states of PO_4-P concentration in wastewater φ_k while the next transition will be done to the state φ_l, $k,l = 1,2,\ldots,v$, $k \neq l$ is denoted by θ_{kl}. Thus the process of PO_4-P concentration in wastewater $\Phi(t)$, $t \in \langle 0, +\infty)$ is described by the following parameters that can be evaluated by expert or identified statistically using the methods (Bogalecka 2020, 2021; Bogalecka & Dereszewska 2022; Grabski 2015; Iosifescu 1980; Kołowrocki 2014; Kołowrocki & SoszyńskaBudny 2011; Limnios & Oprisian 2005; Rice 2007; Smith 1955):

- the matrix of probabilities $[p_{kl}]_{vxv}$ of the process of PO_4-P concentration in wastewater $\Phi(t)$, $t \in \langle 0,+\infty)$ transitions between the states of PO_4-P concentration in wastewater φ_k and φ_l,

$$p_{kl},\ k, l = 1,2,\ldots,v,\ k \neq l \tag{1.1}$$

where $\forall k = 1,2,..., v$, $\theta_{kk} = 0$,

- the matrix of mean values $[M_{kl}]_{v\mathrm{x}v}$ of the process of PO_4-P concentration in wastewater $\Phi(t)$, $t \in \langle 0, +\infty)$ conditional sojourn times θ_{kl} at the state of PO_4-P concentration in wastewater φ_k while its next transition will be done to the state φ_l, $k, l = 1,2,\dots, v$, $k \neq l$,

$$M_{kl} = E[\theta_{kl}] = \int_0^\infty t dH_{kl}(t) = \int_0^\infty t dh_{kl}(t), k, l = 1,2, \dots, v, k \neq l, \qquad (1.2)$$

where $\forall k = 1,2,\dots, v$, $M_{kk} = 0$, and where

$$H_{kl}(t) = P(\theta_{kl} < t), t \in \langle 0,+\infty), k, l = 1,2,\dots, v, k \neq l, \qquad (1.3)$$

are the conditional distribution functions of the process of PO_4-P concentration in wastewater $\Phi(t)$, $t \in \langle 0,+\infty)$ conditional sojourn times θ_{kl}, $k, l = 1,2, \dots, v$, $k \neq l$, at the particular states corresponding to conditional density functions

$$h_{kl}(t) = \frac{dH_{kl}(t)}{dt}, t \in \langle 0, +\infty), k, l = 1,2, \dots, v, k \neq l, \qquad (1.4)$$

- the vector of mean values $[M_k]_{1\mathrm{x}v}$ of the process of PO_4-P concentration in wastewater $\Phi(t)$, $t \in \langle 0, +\infty)$ unconditional sojourn times θ_k, $k = 1,2,\dots, v$, at the states of PO_4-P concentration in wastewater

$$M_k = E[\theta_k] = \sum_{l=1}^{v} p_{kl} M_{kl}, k = 1,2, \dots, v, \qquad (1.5)$$

where p_{kl} and M_{kl} are defined by (1.1) and (1.2) respectively,

- the vector $[p_k]_{1\mathrm{x}v}$ of limit values of transient probabilities

$$p_k(t) = P(\Phi(t) = \varphi_k), t \in \langle 0,+\infty), k = 1,2, \dots, v, \qquad (1.6)$$

of the process of PO_4-P concentration in wastewater $\Phi(t)$, $t \in \langle 0,+\infty)$ at the particular states φ_k, $k = 1,2,\ldots,v$, where

$$p_k = \lim_{t\to\infty} p_k(t) = \frac{\pi_k M_k}{\sum_{l=1}^{v} \pi_l M_l}, k = 1,2, \ldots, v, \tag{1.7}$$

and M_k, $k = 1,2,\ldots,v$, are given by (1.5), and the probabilities π_k, $k = 1,2,\ldots,v$, satisfy the system of equations

$$\begin{cases} [\pi_k] = [\pi_k][p_{kl}] \\ \sum_{l=1}^{v} \pi_l = 1 \end{cases} \tag{1.8}$$

where

$$[\pi_k] = [\pi_1,\pi_2,\ldots,\pi_v],$$

and $[p_{kl}]$ is given by (1.1),

- the vector $[\widehat{M}_k]_{1\mathrm{x}v}$ of the mean values of the total sojourn times $\hat{\theta}_k$, $k = 1,2, \ldots, v$,

$$\widehat{M}_k = E[\hat{\theta}_k] \cong p_k \theta, \tag{1.9}$$

at the particular states φ_k, $k = 1,2,\ldots,v$ of the process of PO_4-P concentration in wastewater $\Phi(t)$, $t \in \langle 0, +\infty)$ in the fixed time interval $\langle 0,\theta\rangle$, $\theta > 0$, where p_k are given by (1.7).

1.2. Application of process of phosphate concentration in wastewater

Using backgrounds given in Section 1.1, the proposed process of PO_4-P concentration in wastewater is applied to identify and predict the PO_4-P concentration in the municipal wastewater collecting in the exemplary wastewater treatment plant in Swarzewo, situated in Pomerania – the north and seaside part of Poland (Fig. 1).

Figure 1. Location of *Swarzewo* Wastewater Treatment Plant (the service area is marked with the red rectangle.

This plant collects sewage from the Puck District and serves around 70 thousand people. Due to the tourist character of this area, the mentioned wastewater treatment plant treats up to 15,000 m^3 of sewage per day in summer and around 5,000 m^3 per day during the other periods. The treated wastewater is discharged into the open waters of the Baltic Sea (Bogalecka & Dereszewska 2022).

The variations of PO_4-P concentration in sewage collected and recorded by *Swarzewo* Wastewater Treatment Plant during the three-years period are presented in Figure 2. The concentrations of PO_4-P are in the range of values recorded for typical municipal wastewater with an average value amounts to 25.8 g/m^3 (Tchobanoglous et al., 2014). The high PO_4-P concentration has only been recorded a three times during the experimental time: more than 60 g/m^3 has been maintained for no more than 24 hours.

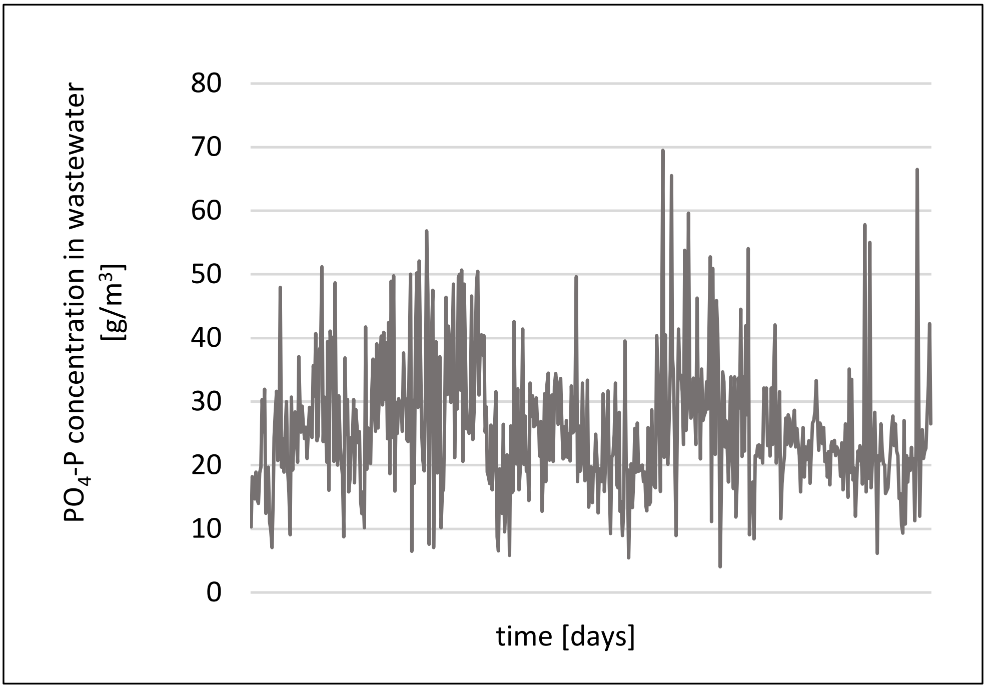

Fig. 2. Variations of phosphate concentration in sewage collected by *Swarzewo* Wastewater Treatment Plant

Source: [own work based on three-years period data].

2. Results

Under the assumption that PO_4-P concentration in wastewater changes over time and taking into account the opinion of experts, the following $v = 3$ particular states of PO_4-P concentration (expressed in g/m^3) in wastewater φ_k, $k = 1,2,3$ of the process of phosphate concentration in wastewater $\Phi(t)$, $t \in \langle 0,+\infty)$ are distinguished and they are as follows:

φ_1 – the phosphate concentration in wastewater belongs to the interval $\langle 0,15)$,

φ_2 – the phosphate concentration in wastewater belongs to the interval $\langle 15,40)$,

φ_3 – the phosphate concentration in wastewater belongs to the interval $\langle 40,+\infty)$.

Next, on the basis of statistical data (coming from the exemplary treatment plant presented in Section 1.1) and collected during the three-years period, the matrix $[n_{kl}]_{3x3}$, $k, l = 1,2,3$, $k \neq l$, of realizations of numbers of the process of PO_4-P concentration in wastewater $\Phi(t)$, $t \in \langle 0,+\infty)$ transitions from the state φ_k into the state φ_l, $k, l = 1,2,3$, $k \neq l$, during the experimental time is fixed as follows:

$$[n_{kl}] = \begin{bmatrix} 0 & 41 & 2 \\ 37 & 0 & 47 \\ 5 & 44 & 0 \end{bmatrix} \qquad (2.1)$$

and the vector $[n_k]_{1x3}$, $k = 1,2,3$, of realizations of the total numbers of the process of PO_4-P concentration in wastewater $\Phi(t)$, $t \in \langle 0,+\infty)$ transitions from the particular state of PO_4-P concentration in wastewater φ_k, $k = 1,2,3$, during the experimental time is

$$[n_k] = [43 \quad 84 \quad 49]. \qquad (2.2)$$

The statistical data for the conditional sojourn times θ_{kl}, $k,l = 1,2,3$, at the states of PO_4-P concentration in wastewater φ_k when the next one is φ_l, $k,l = 1,2,3$, $k \neq l$, are given in Figure 2.

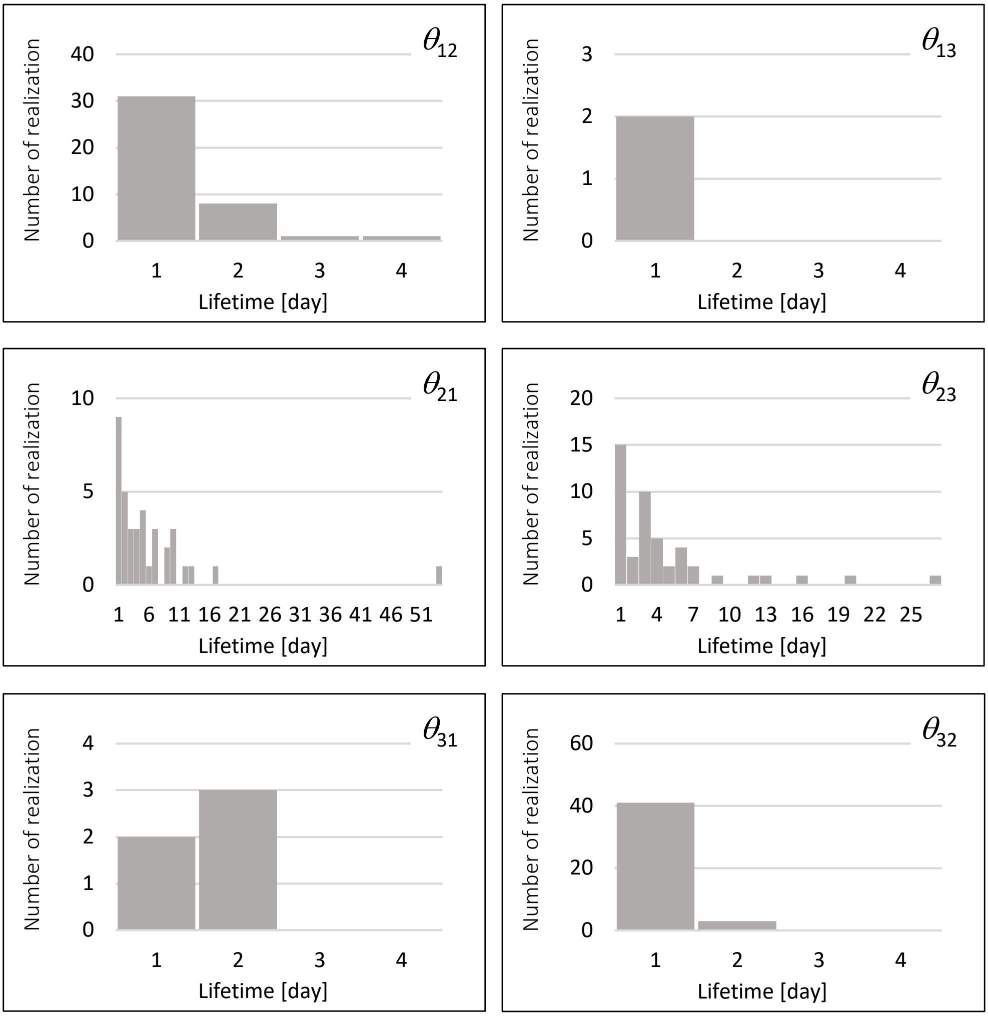

Fig. 3. Graphical representation of statistical data for conditional sojourn times of process of phosphate concentration in wastewater

Source: [own work].

Considering data given in (2.1) and (2.2), the probabilities p_{kl}, $k,l = 1,2,3,\ k \neq l$, of the process of PO_4-P concentration in wastewater transitions between its particular states φ_k and φ_l, $k, l = 1,2,3,\ k \neq l$, are evaluated according to the formula

$$p_{kl} = \frac{n_{kl}}{n_k},\ k, l = 1,2,3,\ k \neq l. \tag{2.3}$$

Thus, the matrix $[p_{kl}]_{3x3}$, $k,l = 1,2,3,\ k \neq l$, of probabilities of the process $\Phi(t)$, $t \in \langle 0,+\infty)$ transitions between its particular states φ_k and φ_l, $k,l = 1,2,3,\ k \neq l$, defined by (1.1), takes the following form:

$$[p_{kl}] = \begin{bmatrix} 0 & 0.95 & 0.05 \\ 0.44 & 0 & 0.56 \\ 0.10 & 0.90 & 0 \end{bmatrix}. \tag{2.4}$$

Using the results and the statistical data coming from the operation process of the exemplary treatment plant presented in Section 1.1 and the procedure and the formulae given in (Bogalecka, 2020, Bogalecka & Dereszewska 2022, Kołowrocki & Soszyńska-Budny, 2011, Rice, 2007), it is possible to evaluate the matrix $[h_{kl}(t)]_{3x3}$ of density functions of conditional sojourn times θ_{kl}, $k, l = 1,2,3,\ \ k \neq l$ of the process $\Phi(t)$, $t \in \langle 0,+\infty)$ at particular states φ_k, $k = 1,2,3$. The forms of density functions $h_{kl}(t)$ defined by (1.4) are identified as follows:

- the conditional sojourn time θ_{12} has the chimney distribution expressed by the density function

$$h_{12}(t) = \begin{cases} 0 & t < 0.7 \\ 1.260 & 0.7 \leq t < 1.3 \\ 0.081 & 1.3 \leq t < 4.3 \\ 0 & t \geq 4.3 \end{cases} \tag{2.5}$$

- the conditional sojourn time θ_{13} has the uniform distribution expressed by the density function

$$h_{13}(t) = \begin{cases} 0 & t < 0.5 \\ 1 & 0.5 \le t < 1.5 \\ 0 & t \ge 1.5 \end{cases} \tag{2.6}$$

- the conditional sojourn time θ_{21} has the chimney distribution expressed by the density function

$$h_{21}(t) = \begin{cases} 0 & t < 0 \\ 0.084 & 0 \le t < 10.6 \\ 0.002 & 10.6 \le t < 63.6 \\ 0 & t \ge 63.6 \end{cases} \tag{2.7}$$

- the conditional sojourn time θ_{23} has the exponential distribution expressed by the density function

$$h_{23}(t) = \begin{cases} 0 & t < 0 \\ 0.218 \exp(-0.218t) & t \ge 0 \end{cases} \tag{2.8}$$

- the conditional sojourn time θ_{31} has the empirical distribution expressed by the density function

$$h_{31}(t) = \begin{cases} 0 & t < 1 \\ 2/5 & 1 \le t < 2 \\ 0 & t \ge 2 \end{cases} \tag{2.9}$$

- the conditional sojourn time θ_{32} has the chimney distribution expressed by the density function

$$h_{32}(t) = \begin{cases} 0 & t < 0.915 \\ 54.823 & 0.915 \le t < 0.932 \\ 0.002 & 0.932 \le t < 2.105 \\ 0 & t \ge 2.105. \end{cases} \tag{2.10}$$

Further, for distributions given by (2.5)-(2.10), the matrix $[M_{kl}]_{3x3}$, $k, l = 1,2,3$, $k \neq l$ of the mean values of the process $\Phi(t)$, $t \in \langle 0,+\infty)$ conditional sojourn times θ_{kl}, $k, l = 1,2,3$, $k \neq l$ at the particular states, defined by (1.2), takes the following form

$$[M_{kl}] = \begin{bmatrix} 0 & 1.44 & 1 \\ 8.73 & 0 & 4.60 \\ 1.60 & 0.96 & 0 \end{bmatrix}. \quad (2.11)$$

This way the process of PO_4-P concentration in wastewater $\Phi(t)$, $t \in \langle 0,+\infty)$ is identified and further its main characteristics can be predicted.

Namely, applying (1.5) and considering (2.4) and (2.11) the approximate mean values of unconditional sojourn times of variables θ_{kl}, $k, l = 1,2,3$, $k \neq l$ can be evaluated

$$M_1 = p_{12}M_{12} + p_{13}M_{13} = 0.95 \cdot 1.44 + 0.05 \cdot 1 = 1.37 + 0.05 = 1.42,$$
$$M_2 = p_{21}M_{21} + p_{23}M_{23} = 0.44 \cdot 8.73 + 0.56 \cdot 4.60 = 3.84 + 2.58 = 6.42,$$
$$M_3 = p_{31}M_{31} + p_{32}M_{32} = 0.10 \cdot 1.60 + 0.90 \cdot 0.96 = 0.16 + 0.86 = 1.02.$$

Thus, the vector $[M_k]_{1x3}$, $k = 1,2,3$, of mean values of the process of PO_4-P concentration in wastewater $\Phi(t)$, $t \in \langle 0,+\infty)$ unconditional sojourn times θ_k, $k = 1,23$, at its particular states φ_k takes the following form

$$[M_k] = [1.42 \quad 6.42 \quad 1.02]. \quad (2.12)$$

Further, to find the limit values of the transient probabilities p_k, $k = 1,2,3$ at particular states of the process $\Phi(t)$, $t \in \langle 0,+\infty)$, the system of equations, according to (1.8), has to be solved. After considering (2.4) it takes the following form

$$\begin{cases} \pi_1 = 0.44\pi_2 + 0.10\pi_3 \\ \pi_2 = 0.95\pi_1 + 0.90\pi_3 \\ \pi_3 = 0.05\pi_1 + 0.56\pi_2 \\ \pi_1 + \pi_2 + \pi_3 = 1 \end{cases} \quad (2.13)$$

whereas its approximate solution is given as the vector $[\pi_k]_{1x3}$, $k = 1,2,3$

$$[\pi_k] = [0.239 \quad 0.480 \quad 0.281]. \tag{2.14}$$

Hence, according to (1.7) and considering (2.12), the vector $[p_k]_{1x3}$ of approximate limit values of the transient probabilities p_k, $k = 1,2,3$, at the particular states φ_k of the process $\Phi(t)$, $t \in \langle 0, +\infty)$ is

$$[p_k] = [0.092 \quad 0.831 \quad 0.077]. \tag{2.15}$$

Finally, by (1.9) and considering (2.15), the vector $\left[\hat{M}_k\right]_{1x3}$ of approximate mean values of the sojourn total time $\hat{\theta}_k$ of the process $\Phi(t)$, $t \in \langle 0, +\infty)$ in the fixed time interval $\theta = 1$ year (365 days) at the particular states φ_k, $k = 1,2,3$, expressed in days, is as follows (Fig. 4):

$$\left[\hat{M}\right] = [33.41 \quad 303.37 \quad 28.22], \tag{2.16}$$

or expressed as a part of a year, is as follows

$$\left[\hat{M}\right] = [0.09 \quad 0.83 \quad 0.08]. \tag{2.17}$$

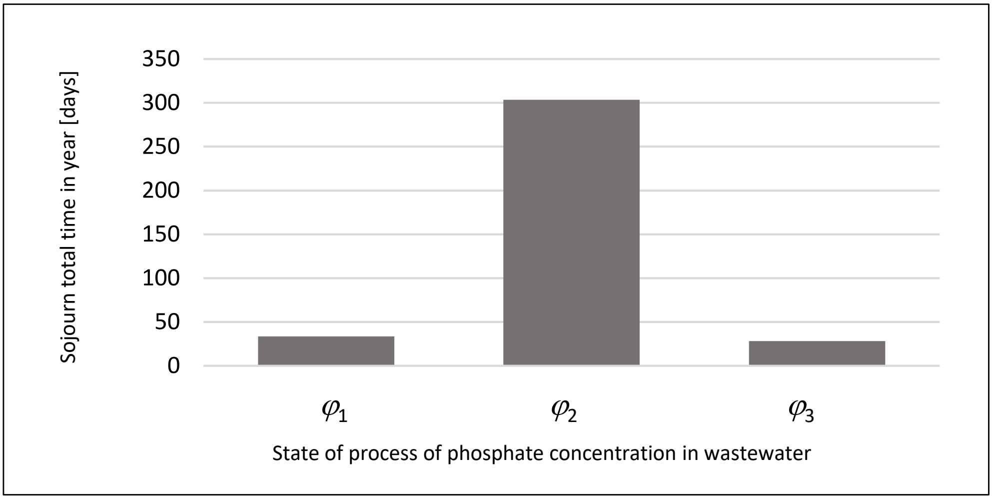

Fig. 4. Approximate mean values of sojourn total time of process of phosphate concentration in wastewater at particular states in 1 year interval

Source: [own work].

3. Discussion

Based on the study, it is determined that the wastewater flowing into the *Swarzewo* WWTP is most often (303.37 days per year) in the state . This means that most often the phosphate concentration is in the range of 15 g/m^3 to 40 g/m^3. These concentrations do not exceed the typical values recorded in municipal wastewater (40-60 mg/m^3). In the case of a wastewater treatment plant using chemical phosphorus removal (such technology is used at *Swarzewo* WWTP), the developed model facilitates estimation of the amount of coagulant necessary to remove phosphorus from wastewater and determination of annual expenses that the wastewater treatment plant must secure for this purpose. These concentrations are not dangerous to the environment if pipeline damage occurs and periodic infiltration of untreated wastewater into the soil. On the other hand, they pose a threat if they were to directly enter the surface water environment.

Conclusions

In the paper, the semi-Markov model of the process of phosphate concentration in wastewater is presented as a novel approach to assess the wastewater quality. The proposed methods provides to obtain the limit values of transient probabilities as well as the approximate mean values of the sojourn total times staying at the established phosphate concentration states. These variables predicted using the semi-Markov model are different from those directly estimated from real data, especially when distributions of the phosphate concentration conditional sojourn times are different from exponential. Thanks to this the prediction of the characteristics of the process of PO_4-P concentration in wastewater is more precise. These results can also be applied to the optimization of PO_4-P concentration in wastewater based on linear programming.

The obtained results can be essential for some authorities responsible to making decision in wastewater treatment plants. Moreover, the proposed model is a universal tool that can be used to assess the quality of other industrial liquids which components concentration is changing in time.

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MUNICIPAL WASTE MANAGEMENT IN POZNAN AGGLOMERATION

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Abstract
The consumer lifestyle contributes to the improvement of the quality of our functioning, but at the same time it is conducive to the production of many different types of waste, including very hazardous industrial and municipal waste. Municipal waste, i.e. waste generated in households, deserves special attention. In 2020, almost 13.1 million tonnes of municipal waste were generated, i.e. an average of 342 kg per capita in 2020, which means an increase by 10 kg compared to the 2019. This paper presents an analysis of the municipal waste management in Poznan agglomeration in 2020 and 2021.

Keywords: municipal waste, waste management, waste segregation

1. Introduction

Waste is all substances or objects created as a result of human activity, as well as the residues of their production, which the holder gets rid of, intends to get rid of or is obliged to get rid of them. The amount and variety of waste produced by people raises concerns and points to a serious civilization problem [Das et al 2019, Yao et al. 2019].

Municipal waste is waste generated in households and directly related to non-industrial human activity. Municipal waste is also called household waste. According to the data of the Central Statistical Office in Poland, almost 13.1 million tons of municipal waste was generated in 2020. The mass of collected waste was nearly 3 percent higher than in the previous year. It means that every Pole generated an average of 342 kg of municipal waste 2020, which means an increase by 10 kg compared to the 2019 [Kostecka et al. 2014, Wieczorek, Siekierski 2021, GUS-Bank Danych Lokalnych].

Unreasonable handling of waste, including its incineration or uncontrolled storage, is a threat to the environment. It causes air, water and soil pollution. The health of humans and other organisms is also endangered. Rational waste management is one of the greatest challenges of the 21st century [Zhang et al. 2021, Kostecka et al. 2014, Wieczorek, Siekierski 2021].

Waste management is a series of processes related to the collection, processing and supervision of such activities, as well as subsequent handling of waste disposal sites and activities performed as a waste seller or waste broker. Waste management is one of the most serious problems in modern civilization. The waste management process is divided into stages, including collection, transport, disposal, recycling and monitoring of waste generated by human activities and other activities. The generation of waste is the most serious problem in the world due to the growing number of population, with economic and technical development, man has become the largest producer of waste in nature. Waste is divided into industrial and municipal waste depending on the place of its generation [Minelgaite, Liobikiene 2019, Zhang et al. 2021].

This paper presents an analysis of the municipal waste management in Poznań agglomeration in 2020 and 2021.

2. Organisational-legislation conditions on waste management in Poznan agglomeration

In Poland the organization of municipal waste management in community is based on the principles set out in the Act of 13 September 1996 on maintaining cleanliness and order in communes [Smol et al. 2020, Act of 13 September 1996]. The Act of 1 July 2011 to amend the law on maintaining cleanliness and order in communes introduced regulations, which have become the basis of the new farming system of municipal waste [Act of 11 July 2011]. The new regulations have been implemented and taken effect from 1 July 2013. The purpose of introducing the new municipal waste management system in community was:

- sealing the municipal waste management system;
- conducting selective collection of municipal waste (raw materials) "at the source";
- reducing the amount of municipal waste sent for landfilling, including biodegradable waste;
- increasing the number of modern installations for waste recovery;
- eliminate illegal landfills and reduce environmental pollution of waste;
- reducing the risks associated with the transport of waste from the places where it is generated to the recovery/disposal sites by creating waste management regions.

These goals resulted from EU regulations, in particular from the Waste Framework Directive and the Waste Storage Directive [Directive (EU) 2018/851, Directive 1999/31/EC].

In accordance with the law on maintaining cleanliness and order in communes, communes ensure cleanliness and order on their territory and create the necessary conditions for them maintenance. According to these management principles, the commune is to organize, manage and exercise control over the waste management system in its area. The commune is also responsible for achieving specific levels of preparation for reuse and recycling of municipal waste and the reduction of the amount of biodegradable waste sent for landfilling. There is a risk of financial sanctions for failure to achieve the indicators and failure to comply with the obligation imposed by the act. According to the definition, waste management includes collection, transport and processing of waste [Minelgaite, Liobikiene 2019, Zhang et al. 2021, Act of 14 December 2012].

The scope of activities related to waste management, includes, among others:

- construction, maintenance and operation of installations for the treatment of municipal waste, including municipal installations;
- coverage of all property owners on the site municipalities with the municipal waste management system;

- supervision of municipal waste management, including the implementation of tasks entrusted to entities collecting municipal waste from property owners;
- ensuring selective collection of municipal waste, including at least: paper, metals, plastics, glass, multi-material packaging waste and bio-waste;
- creation of selective collection points of municipal waste;
- the ability to create and maintain repair points and reuse products or parts of non-waste products;
- conducting information and educational activities in the field of proper municipal waste management, in particular in the field of selective collection of municipal waste;
- providing information on entities collecting municipal waste from property owners from a given commune on the website of the office;
- carrying out an annual analysis of the state of municipal waste management in order to verify the technical and organizational capabilities of the commune in the field of municipal waste management.

According to legislation in applied in Poland the municipal waste is selectively collected and it is categorised into the following fractions [Kulisz and Kujawska 2020, Przydatek 2020]:

- paper, including cardboard and paper packaging waste;
- glass, including glass packaging waste;
- plastics and metals, including plastic or metal packaging waste and multi--material packaging waste;
- biodegradable waste, particularly bio-waste.

The requirement of separate waste collection is fulfilled if the containers and bags ensure that the waste fraction intended for processing is protected against quality deterioration due to, e.g., weather conditions or unauthorized persons [Latosińska et al. 2020, Przydatek 2020].

The evaluation of the municipality’s waste management depends to a large extent on an effective collection of waste and currently on a selective collection as well. The content of municipal waste depends to a large extent on the area urbanization degree from where the waste comes [Sentera et al. 2019, Kulisz and Kujawska 2020, .

In Poznan agglomeration the waste management is carried out by The Inter-Communal Association "Waste Management of the Poznan Agglomeration" (ZM GOAP), which was established in 2010 by ten municipalities near Poznan. Its statute was registered on September 30, 2010. In the spring of 2012, local governments introduced changes to the statute, adjusting it to the requirements of the act and adding permissions enabling the Inter-Communal Association to effectively waste manage. Since January 1, 2014, the commune of Suchy Las has not been a member of the association. The member communes are situated in the poviats of Poznan and Oborniki. The total area of the union covers an area of 1,469.53 km^2 [GOAP].

Under the statute, the union is responsible for organizing the municipal waste management system for all municipalities - union members, including for the collection and management of waste and the organization of selective collection points for municipal waste.

In March 2017, the Assembly of the ZM GOAP adopted resolution No. XXVII/184/2017 on the division of the area of the Inter-Communal Association of Poznan Waste Management Agglomeration into municipal waste collection sectors [GOAP].

According to the adopted amendmentsince since January 1, 2018, the union's area has been divided into 15 municipal waste collection sectors. Sectors 1-7 are sectors located in Poznań, while sectors 8-15 are sectors located in neighboring municipalities (Fig. 1).

Since 2014, the Inter-Communal Association "Waste Management of the Poznan Agglomeration" has been consisted of nine communes:

- the Poznan city (sectors I-VII);
- the city and commune of Buk (sector VIII) ;
- the commune of Oborniki (sector IX);
- the city and commune of Murwana Goslina (sector X);
- the commune of Czerwonak (sector XI);
- the city and commune of Swarzędz (sector XII);
- the city and commune of Pobiedziska (sector XIII);
- the commune of Kleszczewo (sector XIV);
- the city and commune of Kostrzyn (sector XV).

From 1 July 2013, the obligation to organize a municipal waste collection system was covered by municipalities or inter-municipal associations (in the case of transfer of competences by the municipality to the association). The GOAP Inter-Commune Association covered the municipal waste system, including mixed waste, green waste and waste collected separately. Municipal waste was collected from the premises of inhabited and uninhabited properties by companies with which GOAP signed a contract. Other municipal waste, such as, for example, construction and demolition waste, were collected on individual contracts by companies with an entry in the register of regulated activities or were handed over by residents to selective municipal waste collection points [Act of 13 September 1996, GOAP].

Fig. 1. Map of the Inter-Communal Association „Waste Management of the Poznan Agglomeration”

Source: [GOAP].

3. Material and methods

In Polish public statistics, data concerning selective waste collection, recovery and recycling level is obtainable only on the voivodeship level. To have more detailed information one must contact particular local self-governments directly and study annual reports on the issue. The analysis was prepared on the basis of data contained in the annual reports of entities collecting municipal waste from property owners, annual reports of entities running a Municipal Waste Selective Collection Point and annual reports of entities collecting municipal waste. The article also concerns data from the annual reports of the Inter-Communal Association GOAP and the Central Statistical Office (GUS), which show the share of selectively collected waste, including waste, as well as construction selectively collected waste in Poznan agglomeration.

To evaluate the level of municipal waste management (both mixed and selected) in Poznan agglomeration, two rates were proposed [Alankiewicz 2009]:

$$W_1 = \frac{SW_{1inh.}}{MW_{1inh.}} \quad (3.1)$$

where:

$SW_{1inh.}$ – the mass of selected waste per 1 inhabitant [kg/inh./year],

$MW_{1inh.}$ –the mass of mixed waste collected per 1 inhabitant [kg/inh./year].

$$W_2 = \frac{MW_{1inh.} - SW_{1inh.}}{SMW_{1inh.}} \quad (3.2)$$

where:

$MW_{1inh.}$ and $SW_{1inh.}$ – as in Formula 3.1,

$SMW_{1innh.}$ – the mass of municipal waste collected (together mixed and selected) per 1 inhabitant [kg/inh./year].

W_1 rate can theoretically take the value in the $<0,\infty)$ range. Value 0 will be reached when $SW_{1inh.}$ is 0, so there will be no waste selectively collected – the situation extremely undesirable. W_1 rate increases with the increase of the mass of selected waste and the decrease of the mass of mixed waste. W_1 = 1 value will mean that the mass of mixed waste per 1 inhabitant is the same as the mass of selected waste. The more above 1 the W_1 rate gets, the more effective the waste management is.

W_2 rate can take the value in the <-1,1> range. The value -1 reflects the perfect condition when all waste is selectively collected. The value 0 indicates the condition in which the mixed waste mass equals the selected waste mass. The value 1 is the extremely undesirable condition, i.e. when all the waste is collected as mixed.

4. Results and discussion

According to the data of the Central Statistical Office, the number of inhabitants of the of Inter-Communal Association (GOAP) was 724,825 and 722,984 in 2020 and 2021, respectively. Detailed information on the population number based on the Central Statistical Office data is presented in Table 1. The population inhabiting the area of the intercommunal union decreased by 22,000 people in a year, which reflects the nationwide demographic trend in Poland.

Table 1. Population in the Inter-Communal Association (GOAP) in 2020 and 2021 according to the Central Statistical Office

Territorial unit	2020			2021		
	City	**Village**	**Total**	**City**	**Village**	Total
Buk	5,997	6,687	12,664	5,951	6,747	12,698
Czerwonak	-	27,697	27,697	-	27,776	27,776
Kleszczewo	-	9,104	9,104	-	9,589	9,589
Kostrzyn	9,691	8,919	18,610	9,681	9,207	18,888
Murowana Goślina	10,425	6,497	16,922	10,380	6,548	16,928
Oborniki	17,972	16,211	34,183	17,747	16,418	34,165
Pobiedziska	9,407	10,479	19,886	9,470	10,560	20,030
Poznań	533,830	-	533,830	530,464	-	530,464
Swarzędz	30,098	21,831	51,929	29,663	22,783	52,446
Total	**617,400**	**107,425**	**724,825**	**613,356**	**109,628**	**722,984**

Source: own study based on GUS [GUS].

The percentage part of inhabitants of individual communes in the population structure of an Inter-Communal Association is shown in Figure 2.

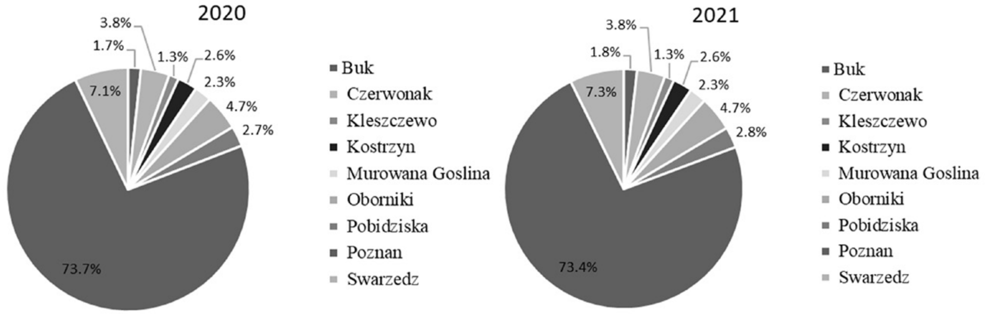

Fig. 2. Part of particular communes inhabitants in the population structure of the Inter-Communal Association

Source: own study based on GUS [GUS].

Under the concluded contracts, mixed municipal waste, biodegradable waste, with particular emphasis on bio-waste, and waste collected selectively (paper, glass and plastics) were gathered. From the area of the Inter-Communal Association, 290,998.54 Mg and 292,333.18 Mg of municipal waste were collected in 2020 and 2021, respectively. This means an rise by almost 1,500 Mg, while the amount of separately collected waste increased, and the amount of mixed waste decreased. Detailed data is presented in Table 2.

Table 2. Amounts of municipal waste collected selectively in the Inter-Communal Association (GOAP) in 2020 and 2021.

Territorial unit	Mixed waste [Mg]	Waste collected selectively			
		Paper [Mg]	Plastics [Mg]	Glass [Mg]	Biowaste [Mg]
2020					
Buk	3,107.74	205.92	343.54	302.38	1,136.44
Czerwonak	6,283.84	519.38	527.84	613.97	2,743.47
Kleszczewo	3,085.10	262.82	273.98	171.98	1,575.78
Kostrzyn	6,004.40	406.28	373.78	292.90	2,041.64
Murowana Goślina	3,013.84	300.11	315.53	371.87	1,650.63
Oborniki	8,213.94	437.49	716.13	709.58	2,482.17
Pobiedziska	5,529.96	342.78	519.18	535.54	19,886
Poznań	135,062.14	14,051.02	11,393.25	12,272.87	33,078.78
Swarzędz	16,505.13	968.90	1,209.52	878.48	6,004.56
Total	**187,706.09**	**17,494.70**	**15,672.75**	**16,149.57**	**53,975.43**
Total	**290,998.54**				
2021					
Buk	2,848.30	266.67	399.46	350.95	1,298.88
Czerwonak	5,844.40	627.77	688.52	681.74	3,487.15
Kleszczewo	2,527.16	356.00	361.22	279.40	1,355.23
Kostrzyn	4,913.52	531.80	571.04	465.28	2,488.38
Murowana Goślina	3,520.78	413.15	463.73	420.14	2,141.49
Oborniki	8,243.28	578.70	856.21	792.30	3,099.21
Pobiedziska	4,772.42	464.22	741.20	663.10	3,447.98
Poznań	125,673.21	16,169.05	14,262.26	14,083.28	37,716.96
Swarzędz	12,539.84	1,535.82	1,732.70	1,435.68	6,223.60
Total	**170,882.91**	**20,943.18**	**20,076.34**	**19,171.87**	**61,258.88**
Total	**292,333.18**				

Source: own study based on GOAP [GOAP].

For the evaluation, the data from the Local Data Bank of Central Statistical Office and reports of the Inter-Communal Association GOAP concerning municipal waste (mixed and selected waste) as well as information on the population were used. The value of W_1 and W_2 rates was calculated and presented in Table 3.

Table 3. The value of W1 and W2 rates in the Inter-Communal Association (GOAP) in 2020 and 2021.

Territorial unit	2020				2021			
	$SW_{1inh.}$	$MW_{1inh.}$	W_1	W_2	$SW_{1inh.}$	$MW_{1inh.}$	W_1	W_2
Buk	159.61	285.38	0.56	0.283	227.17	184.71	0.813	0.103
Czerwonak	169.47	241.78	0.70	0.176	219.99	207.68	0.944	0.029
Kleszczewo	249.41	336.80	0.74	0.149	263.55	245.27	0.931	0.036
Kostrzyn	169,09	325.97	0.52	0.317	263.87	217.85	0.826	0.096
Murowana Goślina	162.16	239.64	0.68	0.193	212.57	207.9	0.978	0.011
Oborniki	125.49	251.31	0.50	0.334	250.40	163.13	0.651	0.211
Pobiedziska	240.36	285.14	0.84	0.085	245.29	275.91	1.125	-0.059
Poznań	153.77	283.38	0.44	0.392	265.07	174.4	0.658	0.206
Swarzędz	180.13	328.02	0.55	0.291	251.47	220.03	0.875	0.067

Source: own study based on GUS and GOAP [GUS, GOAP].

In 2020 and 2021 the value of W_1 rate was the highest in Pobiedziska, which means that in this area there is a high percentage of selected waste. In all municipalitiesthe, W1 rate was higher in 2021 than 2020, which is caused by an increase in the amount of separately collected garbage and a decrease in the amount of mixed waste. The lowest rate occurred in Poznan and Oborniki due to the fact that there is a large percentage of mixed waste per inhabitant and a small amount of selected waste.

In evaluating the condition of waste management with the use of W_2 rate, similar conclusions were drawn. The value of the rate below zero reached in Pobiedziska means that there is more selected waste than mixed one. W_2 is also low in Murowana Goslina, Czerwonak and Kleszczewo, which proves the high percentage of selected waste in the total amount of municipal waste (both mixed and selected). The highest W_2 rate value was reached in Poznan and Oborniki. It means that in these areas there is a large difference between the mass of mixed waste per inhabitant and the mass of selected waste per inhabitant.

Pursuant to the Act on maintaining cleanliness and order in communes, communes are obliged to achieve for 2020 the level of preparation for reuse and recycling of the following fractions of municipal waste: paper, metals, plastic and glass in the amount of at least 50% by weight. However, from 2021, municipalities are required to achieve the following level of preparation for reuse and recycling of municipal waste, as presented in Table 4 [Act of 13 September 1996 and Journal of Laws of 2021, item 888].

Table 3. Preparation levels for reuse and recycling of municipal waste.

Year	Acceptable level of preparation for re-use and recycling of municipal waste
2021	20%
2022	25%
2023	35%
2024	45%
2025	55%
2026	56%
2027	57%
2028	58%
2029	59%
2030	60%
2031	61%
2032	62%
2033	63%
2034	64%
2035 and each subsequent year	65%

Source: based on [Act of 13 September 1996 and Journal of Laws of 2021, item 888].

The achieved level of recycling and preparation for reuse of the following fractions of municipal waste: paper, metals, plastics and glass for the Inter-Communal Association GOAP in 2020 was 42.52%. In 2021 the obtained level of preparation for reuse and recycling of municipal waste was 39.37%. It means that in 2020 the required level was not achieved, while in 2021 this level was reached. Detailed data on the obtained levels of recycling and preparation for reuse of municipal waste is presented in Figure 3.

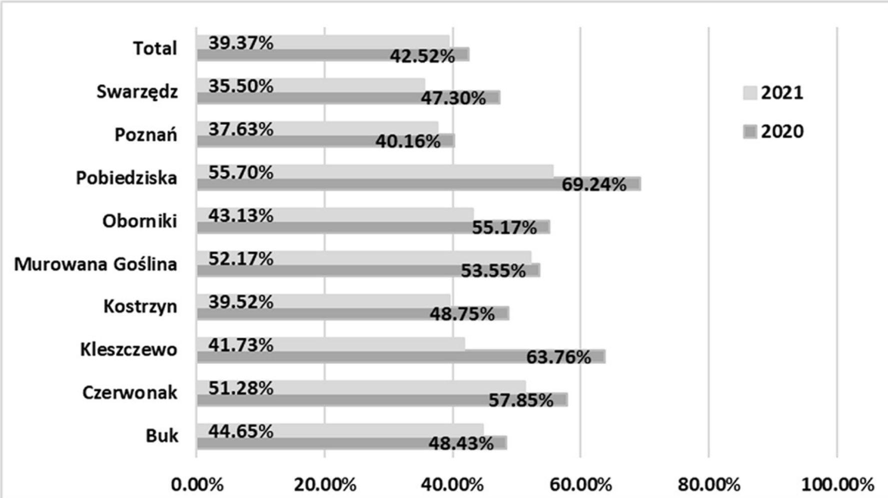

Fig. 3. The level achieved of preparation for reuse and recycling of following fractions of municipal waste: paper, metals, plastics and glass in 2020 and municipal waste in 2021

Source: own study based on GUS and GOAP [GUS, GOAP].

5. Conclusions

The evaluation of the condition of the municipal mixed and selected waste management in Poznan agglomeration with the use of suggested W_1 and W_2 rates allowed for drawing the following conclusions. W_1 rate does not reflect the real level of the collection of selected waste and the condition of waste management as W1 rate value gets zero in each case when selected waste does not occur, regardless of the amount of collected mixed waste (also per one inhabitant). The rate can be used in a comparative assessment of administrative units or in evaluating the same unit in due time. The change of the rate shows the dynamics (tendency) of the relation of the amount of selected waste to mixed waste. The second proposed rate (W_2) determines the differences between mixed waste and selected waste related to all selected municipal waste (both mixed and selected). Only in Pobiedziska, the relation was negative, which means that only there does the mass of selected waste exceed the mass of mixed waste. The rate, just like the previous one, can also be used in a comparative assessment or to show the dynamics of the phenomenon. The level of recycling and preparation for reuse of the municipal waste for the Inter-Communal Association GOAP in 2021 was obtained and compatible with the levels set out in the Act on maintaining cleanliness and order in communes.

It should be noted that the activities in the field of selective waste collection and recovery should be intensified in the coming years so that the implemented regulations serve a consistent waste management policy and affect selective waste collection. An example is the implementation of mandatory selective collection of textiles Art. 11 [Directive (EU) 2018/851] from January 1, 2020, compulsory selective collection of hazardous waste Art 20 [Directive (EU) 2018/851] and mandatory selective collection of at least 77% of plastic bottles Art 9 [Directive (EU) 2019/904], which is a serious challenge for municipalities and local governments.

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PHYTOTOXICITY OF BAMBOO TEXTILE PRODUCTS

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Abstract
In this study, the effect of bamboo textile products introduced into peat on the emergence, growth, and development of plants was determined. In the experiment, seeds of selected plant species - barley and mustard - were sown into pots containing acid and deacidified peat, in which samples of bamboo fibre products had been previously degraded. At the same time, control samples were conducted on peat without the degradation process. To evaluate the phytotoxicity of bamboo fiber products, the emergence, green and dry mass of plants from control samples were determined and compared with the emergence, green and dry mass of plants growing on acidic and deacidified peat in which bamboo fiber product samples had been degraded for eight months previously.

Keywords: phytotoxicity, acid peat, deacidified peat, degradation, bamboo fiber

Introduction

Nowadays, more and more attention is being paid to industrial articles derived from renewable plant raw materials that are declared biodegradable. One of them are cloths made from bamboo fiber for everyday household use. After use, biodegradable products end up in mixed waste or biowaste, where they are turned into compost and then used in agriculture to fertilize plants. Their impact on plants is not always known.

Phytotoxicity is the negative (toxic) effect of a substance on plants, e.g. through the misuse of plant protection products in agrotechnical treatments, i.e. pesticides, herbicides or fungicides. [www.ekologia.pl]

Symptoms of phytotoxicity include: loss of parts or whole crops shortly after emergence, color changes - including localized - and all kinds of plant deformities. Curling, dwarfing and other size and volume deviations involving both above-ground (stems) and below-ground (roots) parts. [www.gov.pl]

Phytotoxic effects of chemicals can be determined by the dynamics of germination, growth seedlings, reduction of dry and fresh mass of roots or coleoptile of test plants. [Sekutowski 2012]

Phytotoxicity tests are performed on monocotyledons (e.g. wheat, barley, rye) or dicotyledons (e.g. mustard, radish, cress). In the present study, tests were carried out on barley and mustard.

Spring barley is characterized by fairly high soil requirements. Due to a poorly developed root system, soil is essential for proper growth: good water storage, warm and with a pH of about 6-6.5. In the early stages of development spring barley is sensitive to excess or deficiency of water. [www.lgseeds.pl]

White mustard requires soils rich in calcium with an appropriate pH, preferably neutral. Its cultivation can be carried out on peaty, permeable and moderately moist soils. Its plants are characterized by very fast growth and a short vegetation period. [www.rynek-rolny.pl]

In the present study, barley and mustard were sown on peats on which bamboo fabric samples had been previously degraded. Bamboo fiber is a cellulose fiber (semi-synthetic fabric) that is regenerated from bamboo. It has various micro-gaps, which makes it softer than cotton. This property increases the ability of this fabric to absorb moisture. Articles made from bamboo fiber are flexible, environmentally friendly and biodegradable. The fiber is bacteriostatic, antifungal, antibacterial, hypoallergenic, hygroscopic, naturally deodorizing and resistant to ultraviolet light. In addition, bamboo is very durable, stable and strong and has significant tensile strength. The bamboo used to prepare the fiber is usually 3-4 years old. Bamboo fiber as a textile material is increasingly being chosen as an alternative to cotton or linen. [www.cosycott.pl]

In this study, the effect of peat-degraded bamboo fibre products on the emergence, growth and development of barley and mustard plants was determined.

1. Material and methods

The research material consisted of cloths used in households, manufactured by "Jan Niezbędny" company, made of bamboo fiber, delicate, absorbent, perforated, declared by the manufacturer as 100% biodegradable material. [www.janniezbedny.pl]

1.1. Degradation

Degradation of bamboo samples was carried out in acidic and deacidified peat in perforated plastic containers in a natural environment. Characteristic parameters of both peats on the basis of manufacturer's data are presented in Table 1.

Table 1. Parameters of horticultural peat used for the study by COMECO S.A. from Płock

Percentage of elements in dry matter	Acidic peat *	Deacidified peat *
Organic carbon (C)	52%	52%
Organic nitrogen (N)	0,2%	0,2%
Organic matter	90%	90%
pH in H2O	3,5-4,5	5,5-6,5**

** hygroscopic material, does not contain fertilizer*

*** peat acidity controlled with chalk*

Source: manufacturer's information [www.comeco.pl]

The perforation allowed free access of water and air to the degraded material. Each container contained 250g of peat and 5 samples (2cm x 15cm) of the degraded material. The bamboo samples accounted for approximately 1.2g per container. Degradation continued for eight months until the samples were completely decomposed.

1.2. Phytotoxicity

The phytotoxicity test consisted of sowing barley grains (a monocotyledonous plant) and mustard seeds (a dicotyledonous plant) in acid and deacidified peat in which degradation of bamboo samples had previously occurred. At the same time, control samples were conducted on peats without degradation process. Twenty barley or mustard seeds were placed in each pot. The plant growth site was warm (about 20°C), sunny and moist. After 14 days the plants were cleaned of peat, counted, measured and weighed.

Inhibition or stimulation was determined by measuring root and stem growth, which were related to control samples.

- **The germination capacity (C_G, %)** was defined by the formula [Franica et al. 2018; Czop et al. 2016]:

$$C_G = \frac{n_g}{n_t} \cdot 100 \quad [\%] \tag{1.1}$$

where:
n_g - number of germinated seeds,
n_t - total number of seeds sown.

- **The plant root growth inhibition factor (I_R, %)** was calculated from the formula [Franica et al. 2018; Czop et al. 2016]:

$$I_R = \frac{L_c - L_t}{L_c} \cdot 100 \quad [\%] \tag{1.2}$$

where:
L_c – average root length of the plants in the control sample [mm],
L_t – average root length of the plants in the test sample [mm].

- **The plant stem growth inhibition coefficient (I_S, %)** was calculated similarly [Franica et al. 2018; Czop et al. 2016]:

$$I_S = \frac{L_c - L_t}{L_c} \cdot 100 \quad [\%] \tag{1.3}$$

where:
L_c – average plant stem length in the control sample [mm],
L_t – average plant stem length in the test sample [mm].

- **The growth inhibition coefficient for the whole plant (I_C, %)** was also calculated:

$$I_W = / I_R / + / I_S / \ [\%] \quad (1.4)$$

where:
I_R – root growth inhibition factor of plants [%],
I_S – stem growth inhibition factor of plants [%].

- **The root growth index (GI_R, %)** for the sum of both parameters was calculated according to the formula [Franica et al. 2018; Czop et al. 2016]:

$$GI_R = \frac{(G_t \cdot L_t)}{(G_c \cdot L_c)} \cdot 100 \quad [\%] \quad (1.5)$$

where:
G_t - number of germinated seeds in the test sample,
G_c - number of germinated seeds in the control sample,
L_t - the length of the roots in the test sample [mm],
L_c - the length of roots in the control sample [mm].

- **The stem growth index (GI_S, %)** for the sum of both parameters was calculated similarly according to the formula:

$$GI_S = \frac{(G_S \cdot L_S)}{(G_c \cdot L_c)} \cdot 100 \quad [\%] \quad (1.6)$$

where:
G_t - number of germinated seeds in the test sample,
G_c - number of germinated seeds in the control sample,
L_t - the length of the stem in the test sample [mm],
L_c - the length of stem in the control sample [mm].

To evaluate the phytotoxicity of bamboo fiber products, the emergence, green and dry mass of plants from control samples were determined and compared with the emergence, green and dry mass of plants growing on acidic and deacidified peat in which bamboo fiber product samples had been degraded for eight months previously [Biczak et al. 2012; Herman et al. 2010].

Visual assessment of all the damage to the test plants such as stunted growth, chlorotic and necrotic lesions was also done.

The determinations of the control and test samples are shown in Table 2.

Table 2. Sample determinations

B/A	barley/acidic peat
B/A/B	barley/acidic peat/bamboo fibre
B/D	barley/deacidifield peat
B/D/B	barley/deacidifield peat/bamboo fibre
M/A	mustard/acidic peat
M/A/B	mustard/acidic peat/bamboo fibre
M/D	mustard/deacidifield peat
M/D/B	mustard/deacidifield peat/bamboo fibre

Source: own study

2. Results and discussion

Based on EN 13432, a substance is considered to exhibit toxicity if the germinated seed rate, plant weight growth and fresh weight of plants growing on a medium with the test substance differ by 10% compared to the control sample.

The germination capacity of barley and mustard sown on acid and deacidified peat after bamboo fiber degradation is shown in Table 3.

Table 3. Germination capacity of barley and mustard sown on acid and deacidified peat after bamboo fiber degradation

Sample	Amount of seeds planted [pcs]	Amount of seeds germinated [pcs]	Germination capacity C_G [%]
B/A	20	16	80
B/A/B	20	17	85
B/D	20	17	85

Sample	Amount of seeds planted [pcs]	Amount of seeds germinated [pcs]	Germination capacity C_G [%]
B/D/B	20	14	70
M/A	20	19	95
M/A/B	20	18	90
M/D	20	17	85
M/D/B	20	15	75

Source: own study

The germination capacity of barley on deacidified peat after degradation of bamboo fiber was reduced by 15% compared to the control sample (max. 10%).

The germination capacity of both barley and mustard on acid peat after degradation of bamboo fibre was within the limits allowed by the standard [PN-EN 13432, EN 14995].

A comparison of barley and mustard root length depending on the type of substrate tested before and after bamboo fiber degradation is shown in Fig. 1.

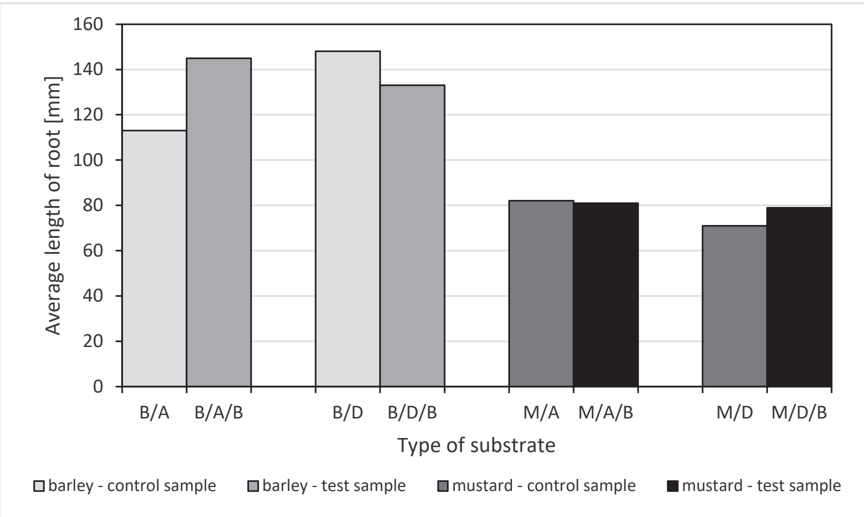

Fig. 1. Comparison of barley and mustard root length according to the type of substrate tested before and after bamboo fiber degradation

Source: own study

Excessive growth of the root zone of barley sown on acid peat after bamboo fiber degradation compared to the control sample was observed.

Both excessive root growth and inhibited root growth are indicative of phytotoxicity.

A comparison of barley and mustard stem lengths according to the type of substrate tested before and after bamboo fiber degradation is shown in Fig. 2.

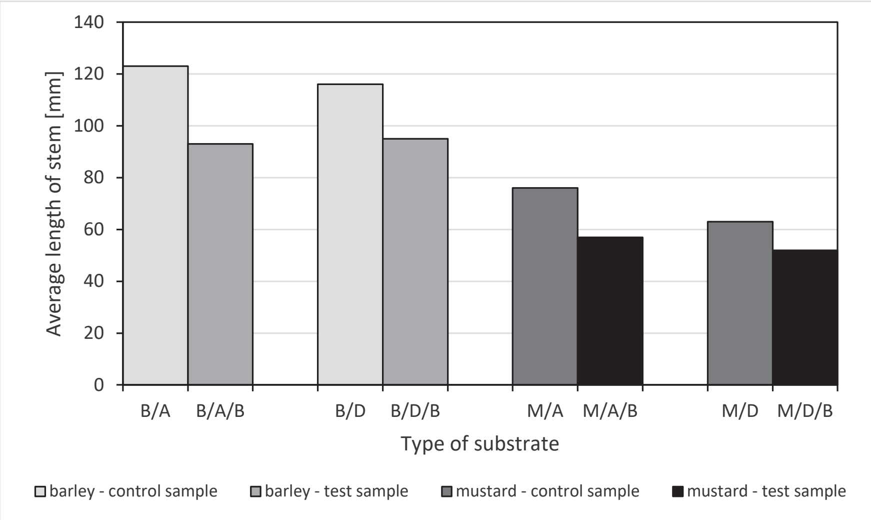

Fig. 2. Comparison of barley and mustard stem lengths according to the type of substrate tested before and after bamboo fiber degradation

Source: own study

The stem length of barley sown on acidic and deacidified peat after bamboo fiber degradation is more than 10% lower compared to the control samples.

The length of mustard stems sown in the same way as barley is well within the standard [PN-EN 13432, EN 14995].

The inhibition coefficient for barley and mustard sown on acid and deacidified peat after bamboo fiber degradation is shown in Table 4.

Table 4. Inhibition coefficient for barley and mustard sown on acid and deacidified peat after bamboo fiber degradation

Sample	Root growth inhibition index I_R [%]	Stem growth inhibition index I_S [%]	Whole plant growth inhibition index I_W [%]
B/A	0	0	0
B/A/B	-28	24	52
B/D	0	0	0
B/D/B	10	18	28
M/A	0	0	0
M/A/B	1	25	26
M/D	0	0	0
M/D/B	-11	17	28

Source: own study

The root growth inhibition coefficient of barley on acid peat after bamboo fiber degradation was exceeded (-28%) - the root system grew excessively.

The growth inhibition coefficient of barley and mustard stems on acid and de-acidified peat after bamboo fiber degradation was also exceeded (17-25%), with weaker plant growth observed on acid peat than on de-acidified peat.

Considering the whole plant (root and stem), exceedance of the acceptable limits of growth inhibition was observed in each case, both for mustard and for barley, with the highest growth inhibition recorded for barley.

The growth index of barley and mustard sown on acid and deacidified peat after bamboo fiber degradation is presented in Table 5.

Table 5. Growth index of barley and mustard sown on acid and deacidified peat after bamboo fiber degradation

Sample	Root growth index GI_R [%]	Stem growth index GI_S [%]
B/A	100	100
B/A/B	136	80
B/D	100	100
B/D/B	74	67
M/A	100	100
M/A/B	94	71
M/D	100	100
M/D/B	98	73

Source: own study

Incorrect root growth index of barley was observed on acidic and de-acidified peat after degradation of bamboo fiber except that on acidic peat the root growth of barley was excessive (136%) while on de-acidified peat the growth was impaired (74%).

The stem growth index of both barley and mustard on acidic and de-acidified peat after degradation of bamboo samples was inhibited, indicating the toxic effect of degraded bamboo material on the test plants.

Changes in basic phytotoxicity test parameters for barley and mustard sown on acid and deacidified peat after degradation of bamboo fiber are presented in Table 6.

Table 6. Changes in basic phytotoxicity test parameters for barley and mustard sown on acid and deacidified peat after degradation of bamboo fiber

Sam-ple	Number of plants [pcs]	% germi-nations relative to the controls	Crop fresh weight [g/pot]	% of crop relative to the control	Average weight of single plant [g]	% of sin-gle plant weight relative to the control	Dry mass [mg/g f.m.]	% of dry mass relati-ve to the control
B/A	16	100	4,05	100	0,25	100	0,0131	100
B/A/B	17	106	3,00	74	0,18	70	0,0142	108
B/D	17	100	4,07	100	0,24	100	0,0125	100
B/D/B	14	82	2,81	69	0,20	84	0,0130	103
M/A	19	100	5,48	100	0,29	100	0,0075	100
M/A/B	18	95	2,66	49	0,15	51	0,0108	145
M/D	17	100	2,52	100	0,15	100	0,0081	100
M/D/B	15	88	1,68	67	0,11	75	0,0089	109

Source: own study

The percentage of yield relative to the control sample on both peats after bamboo fiber degradation was reduced 49-74%.

The average weight of each plant in the tested samples was lower than the control samples, which similarly translates into a reduced percentage of weight per plant relative to the control (51-84%).

An increase in the dry weight of the tested plant samples compared to the control was observed, which can be explained by the lower water content of the tested plants. Lower plant hydration affects the assimilation of nutrients resulting in inhibition of plant growth.

Digital images of barley plants after 14 days of growth on acidic and deacidified peat following bamboo fiber degradation are shown in Table 7.

Chlorotic changes were observed in barley from test versus control samples; necrotic changes were not observed in plants.

Table 7. Digital photographs of barley plants after 14 days of growth on acidic and deacidified peat following bamboo fiber degradation

TEST SAMPLE	CONTROL SAMPLE
	
B/A	B/A/B
	
B/D	B/D/B

Source: own study

Digital images of mustard plants after 14 days of growth on acidic and deacidified peat following bamboo fiber degradation are shown in Table 8.

In mustard, as in barley, sown on both peats after bamboo fiber degradation, chlorotic changes were observed relative to controls; necrotic changes were not observed in plants.

Macroscopic photographs confirm previous results and indicate phytotoxic changes in plant size and chlorophyll staining in monocotyledonous and dicotyledonous plants.

Table 8. Digital photographs of mustard plants after 14 days of growth on acidic and deacidified peat following bamboo fiber degradation

TEST SAMPLE	CONTROL SAMPLE
	
M/A	M/A/B
	
M/D	M/D/B

Source: own study

Conclusions

The phytotoxicity of bamboo fiber on the tested plants: barley and mustard was observed from the study. Barley was more sensitive to phytotoxicity than mustard.

Phytotoxicity in the tested plants manifested among others in dwarfism of the above-ground parts, excessive growth of the root zone and reduced water content in plants, which also led to disturbances in chlorophyll staining.

The bamboo textile used in the study, although decomposable in acidic and deacidified peat, did not have a beneficial effect on the development of mono- and dicotyledonous plants.

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SUITABILITY AS A TOOL FOR MEASURING THE QUALITY OF LIFE IN SELECTED LOCAL GOVERNMENT UNITS OF THE POMERANIAN VOIVODESHIP

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Abstract
Measuring the sustainable development in local government units is of key importance today. The changes that occur around us determine the need for corrective actions aimed at improving the quality of life of the present
and future generations. Issues with defining, analysing and monitoring the changes affect almost all levels of management. Thanks to the total and partial utility tool, these changes can be presented clearly and comprehensibly. Thanks to the division of indicators into stimulants and destimulants, it is possible to determine to what extent the changes in their size have a positive or negative impact on the development of a given agglomeration. The aim of the article is a comparative analysis of selected cities in the Pomeranian Voivodeship using the total and partial utility tools.
The study of selected local government units made it possible to identify opportunities and threats that result from changes in the value of utility, which characterize the quality of life in a broader sense. The conducted research showed that the city of Gdańsk is characterized by the highest degree of sustainability, while the city of Sopot obtained less favourable values of total utility.

Keywords: quality of life, sustainable development, utility, indicators

Introduction

The concept of sustainable development always refers to three harmonized planes: social, economic and environmental. As a result, there is a state of equilibrium that ensures the durability of existing systems, and the disruptions in one are carried over to the other[1]. Such a state means that the development of one of the elements should not interfere with the functioning of other elements. For example, some social and economic phenomena contribute to the degradation of the natural environment.[2]

The implementation of social goal, which is to ensure high, expected quality of life, may have a negative impact on the condition of natural environment. The idea of sustainable development is an objection to negative phenomena occurring in our living environment, which are dangerous for the existence of individuals and for the survival of humanity[3]. Therefore, the overriding goal should be to measure sustainable development at every level. Monitoring of changes with the use of indicators and usability methods will allow for actions leading to the improvement of the quality of life of the inhabitants. A broad analysis of sustainable development indicators may pose many difficulties for local authorities, therefore the use of total and partial utility will allow for a clear and clear interpretation of the data. Only research on changes will allow for the introduction of corrective measures increasing the broadly understood quality of life.

The authors of the research adopted the hypothesis that it is possible to apply the qualitative convention to assess the development changes of local government units treated as objects. It was also assumed that a useful tool for comparing changes in the objective quality of life in selected cities, in terms of social, economic and environmental order, apart from the indicators of sustainable development, may also be the value of partial utility and total.

[1] Kryk B., *Ekorozwój jako przyjęta koncepcja rozwoju społeczno-ekonomicznego a inwestycje ekologiczne*, „Prace Katedry Mikroekonomii" 2003, nr 8, „Zeszyty Naukowe Uniwersytetu Szczecińskiego" 2003, nr 367

[2] Smutek J., *Suburbanizacja, rozwój niezrównoważony i jego konsekwencje dla wydatków gmin w Polsce*, Handel wewnętrzny, tom II, Trendy i wyzwania zrównoważonego rozwoju XXI wieku, 2012

[3] Sztumski W., *PROBLEMY EKOROZWOJU* – PROBLEMS OF SUSTAINABLE DEVELOPMENT 2008, vol. 3, No 2, str. 133-139

1. Material and methods

Measuring the sustainable development in Local Government Units is of crucial importance today. The changes that are taking place around us determine the need for corrective actions aimed at improving the quality of life of the present and future generations. Issues with determining, analyzing and monitoring the changes affect almost all levels of management. Thanks to the tool of total and partial utility, these changes can be presented in a clear and understandable way. By dividing the indicators into stimulants and destimulants, it is also possible to determine whether they actually have a positive or negative impact on further development. Whether an increase or decrease in their value requires a simple or multidimensional analysis. It is worth noting that the indication whether a given indicator is a stimulant or a destimulant is not always obvious.

Three cities with poviat rights of the Pomeranian Voivodeship were selected for research in this study: Gdańsk, Sopot and Gdynia. These cities are comparable in terms of their per capita income, and they are homogeneous Local Government Units. The analysis concerns the quality of life in a broader sense, however, only six indicators were selected for this research.

The population density in this study, defined as a destimulant, i.e. the number of people per given area unit, is the product of two demographic phenomena: natural movement and migratory movement. The first factor includes elements such as births, deaths, marriages and divorces. These elements influence the natural increase in population in a given area. On the other hand, population migration is the second factor . It concerns both migrations within a commune, poviat, voivodeship or country, as well as foreign migrations. The increasing population density determines the suburbanization process.

At present, there are economic reasons for the intensification of suburbanization in Poland, including the uneven use of this phenomenon[4]. The policy of local government units, which often use this process in the first phase, should also be

[4] Bach S., Kloas J., Kuhfeld H., *Wem nutzt die Entfernungspauschale*?, "Informationen zur Raumentwicklung, Heft" 2007, No. 2/3, s. 201-209.

mentioned. In the Polish political system, this applies, inter alia, to real estate tax and income from personal income tax[5].

Excessive suburbanization has a destructive effect on the natural environment, and the implementation of the goal of improving the residents' quality of life may be in contradiction with the requirements of environmental protection.

Another indicator analysed is the amount of municipal waste collected during a year, also referred to as a destimulant. An inherent attribute of households is the generation of municipal waste, which constitutes a macroeconomic, social and political issue. Individual production of such waste by residents in households requires their collective handling (management), and such a task has been made a public utility service. Maintaining cleanliness and order in communes is one of their obligatory tasks[6]. They ensure cleanliness and order in their own areas and create conditions necessary for their maintenance. Municipalities cover all property owners within their municipal waste management system. The processes of producing and managing municipal waste (collection, transport, waste treatment, including the supervision of such activities) are referred to as waste management. Waste management is a complex, interdisciplinary concept; it covers both activities in the field of planning and implementation of projects and technologies as well as their control[7]. Municipal waste management has been - especially since 2013 - the subject of research and numerous scientific publications[8]. They are dominated by the commune perspective , and among the economic and financial issues - research on the ability of households to incur expenditures on municipal waste management services.[9] Another indicator adopted for the study refers to the number of passenger cars per 1000 inhabitants defined as a stimulant. Mobility is

5 Smutek J*., Zmiany dystrybucji przestrzennej dochodów budżetów gmin z tytułu podatku od nieruchomości w obszarach aglomeracji miast wojewódzkich w latach 1995-2009* (w:) Skotarczak T. (red), Zmiany na rynku usług związanych z nieruchomościami, „Studia Prawa i Gospodarki Nieruchomościami", „Seria Monografia 2011.

6 Szelągowska A. , *Miasta w świetle koncepcji zrównoważonego rozwoju,* op. cit., s. 23-30

7 Bogajewski T., *Logistyka zbierania domowych odpadów komunalnych stałych,* Logistyka, 2006 | nr 6 | 76-78

8 Bogajewski T*., Zagospodarowanie odpadów komunalnych w XXI wieku*, Ekoproblemy 4/2001

9 Wąsowicz K., Famielec S., Chełkowski M., *Gospodarka odpadami komunalnymi we współczesnych miastach,* Uniwersytet Ekonomiczny w Krakowie, 2018

essential to ensure freedom of movement and a good quality of life. It is closely related to the concept of sustainable development adopted in urban development and transport strategies. Sustainable development aims to reduce the mobility problems experienced by most of the urbanized areas in Poland. Traffic level and congestion, air pollution, noise, exhaust emissions, consumption of non-renewable resources, social exclusion, urban sprawl and road accidents are significant challenges that require sustainable urban development and transport[10].

The indicator that directly relates to the quality of life in a broader sense is the range of public roads with hard surface per 100 km2. This indicator is directly related to the previous indicator and determines the inhabitants' sustainable mobility, defined in the study as a stimulant. It is worth noting that hard surface roads include roads with improved hard surface (made of stone cubes, clinker, concrete, stone-concrete slabs, bitumen) and roads with unimproved surface (with a gravel and paving surface). Accessibility of roads is one of the most important development aspects, influencing the value of the indicator concerning the length of bicycle paths in the examined cities. Proper planning of the bicycle route network is a basic activity influencing its effective and safe use by the cyclists. Planning the infrastructure for cyclists is an integral part of the transport policy as well as the spatial and social policy.

Therefore, the development of infrastructure network for cyclists and organizational solutions for bicycle traffic should be integrated with the transport policy for all means of transport, and with the overall spatial policy. Infrastructure for cyclists comprises a set of elements of linear infrastructure of various types, calm traffic zones, including residence zones and zones with limited speed up to 30 km / h, and point elements: parking lots, bicycle service areas, creating a coherent system of interrelationships with appropriate road marking.

Another indicator in this analysis is the share of people using social benefits relative to the total population [%], defined as a destimulant. Social Welfare Centers offer many types of services to individuals and families who need permanent

[10] Wyszomirski O., *Zrównoważony rozwój transportu w miastach a jakość życia,* Transport miejski i regionalny 12 2017

or one-time assistance. Social assistance aim to make it possible to overcome difficult life situations, which the said centers are not able to improve with the support they offer, using their rights, resources and possibilities.

The tools used by social assistance include, first of all, social work, various types of benefits, assistance and counseling. Social assistance benefits of a pecuniary nature (pursuant to Article 36 (1) of the Act on Social Assistance) include: permanent allowance, periodic allowance, specific allowance, special purpose allowance, allowance and loan for economic independence, assistance for foster families, assistance for self-empowerment and continuing education for people leaving certain types of care and educational facilities, nursing homes for intellectually disabled children and youth, homes for mothers with underage children and pregnant women, shelters for minors, correctional facilities, special school and education centers, youth centers educational and foster families.

The article uses data collected in the Central Statistical Office database. This analysis proves that it is possible to use the usability method to present research results in an accessible way. The essence of the conversion of sustainable development indicators to the utility indicator is that the mathematical equation used allows to reduce the units characterizing individual indicators and convert them to real numbers in the 0-1 range as partial utility values. Then the obtained values of the real numbers for various indicators can be summarized and, as a total utility value, clearly presented to individual cities.

However, it is crucial to define the function that a given indicator performs, i.e. whether it is a stimulant (S; an increase in its value is favorable), a destimulant (D; an increase in its value is unfavorable) or a nominant (the most favorable values are intermediate values). In this study, the indicators were classified as stimulants or destimulants.

The partial utility is the relative value of the sustainable development index for the analyzed city compared to the values of other cities and is calculated according to the following formula:

$$U_{ij=}\frac{Cij - C_j^0}{C_j^1 - C_j^0}$$

where:

- U_{ij}—partial utility for city *i* relative to indicator *j*,
- C_{ij}—value of sustainable development indicator *j* for city *i*,
- C0j—the lowest (for the sustainable development stimulant) or the highest (for the sustainable development destimulant) value of the sustainable development indicator *j* among the analyzed cities,
- C1j —the highest (for the sustainable development stimulant) or the lowest (for the sustainable development destimulant) value of the sustainable development indicator *j* among the analyzed cities[11].

The value of partial utility falls into the range of real numbers 0–1. When the value is equal to 0, it proves that the given city obtained the worst result among the cities analyzed. On the other hand, when the value of partial utility is 1, it means that the city is the leader in relation to a given indicator[12].

Total utility is calculated using the formula[13]

$$UGi = \sum_{j=1}^{n} Uij$$

The total utility value for a given city depends not only on the value of partial utility, but also on the number of indicators analyzed. With a maximum partial utility value of 1, the total utility value is equal to the sum of indices included in the given analysis[14]

[11] Alpopi C.,. Manole C,. Colesca S. E, *Assessment of the Sustainable Urban Development Level through the Use of Indicators of Sustainability,* "Theoretical and Empirical Researches In Urban Management" 2011, Vol. 6, Iss. 2.

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[13] Alpopi C., Iacoboaea C., Stănescu A., *Analysis of the current housing situation in Romania in the European context,* Faculty of Administration and Public Management, Academy of Economic Studies, Bucharest, Romania, Transylvanian Review of Administrative Sciences , 2011, str. 79-81.

[14] Przybyłowski A. , Kałaska A. , Przybyłowski P., *Quest for a Tool Measuring Urban Quality of Life: ISO 37120 Standard Sustainable Development Indicator*, *Energie* **2022**, *15*(8)

Acceleration of civilization development causes slow depletion of natural resources, impoverishment of biosphere, disturbance of ecological balance and more and more often it brings much destruction, disasters and threats. Our constantly developing scientific and technical civilization faced a serious crisis of a global nature. The fact is that for a long time, human relationships with the nature lead to the growing problems of civilization, manifested in the disturbance of social and biological structure of human existence. Reconciling the development of civilization with the proper functioning of the natural environment is now a complicated and difficult thing[15].

The only alternative to this state of affairs is to continue further civilization development based on the sustainable development. It is worth pointing out that the principles of sustainable development focus on all activities leading to protecting and securing the three elements of development, i.e. society (social aspect), nature (environmental aspect) and economy (economic aspect). In order to achieve the sustainable development assumed goals and improve the quality of life, it is necessary to revaluate the current way of thinking, i.e. to implement these measures, but not to lower the current level of civilization development. Assuming a permanent improvement in the contemporary and future generations quality of life , it is necessary to constantly perform activities aimed to improve the condition of natural environment as an integral part of people's lives.

The concept of sustainable development, based on anthropocentric foundations, aims to improve the present and future human generations' quality of life, while maintaining natural resources in the current state, and in many cases the sustainable development is focused on urban areas. Its subject of interest refers to the natural, social and economic processes, occurring both in the cities themselves and in their surroundings as a result of the phenomena of suburbanization[16],[17].

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[15] Skowroński A., *Zrównoważony rozwój perspektywą dalszego postępu cywilizacyjnego*, Problemy Ekorozwoju, 2006 , I, s. 47-57

[16] Kistowski M., 2008. *Niezrównoważony rozwój aglomeracji trójmiejskiej – problemy i perspektywy.* Problemy Ekologii Krajobrazu, T. XXII. 211–221.

[17] Lorens P. (red.) 2005. *Problemy suburbanizacji*. Biblioteka Urbanisty 7. Urbanista, Warszawa

In recent years, the effects of spatial development and urbanization pressure are particularly visible, resulting in the impoverishment or even destruction of green areas and environmental protection. Unfortunately, it is in cities that the environmental, social and economic orders intersect and that is why it is so important to carry out activities that will not lead to unsustainable development.

2. Results

In this study, the total and partial utility was calculated for six selected indicators of the environmental order, which undoubtedly prove the quality of life in a given city. The list of sustainable development indicators for the cities examined is presented in Table 1.

Table 1. Values of sustainable development indicators for the cities examined

City/ Indicator	2018	2019	2020
Gdańsk			
1. Population density [person per km^2]	1781	1798	1797
2. Municipal waste collected during the year [thousand t]	19,12	19,81	16,50
3. Passenger cars per 1000 population [pcs.]	646,5	670,2	686,4
4. Public roads with hard surface (poviat and communal roads) per 100 km^2 [km]	102,4	104,3	109,1
5. Number of people with social benefits 6. in total population [%]	2,4	2,1	2,1
7. Length of bicycle paths [km]	182	196	203
Gdynia			
1. Population density [person per km^2]	1823	1823	1813
2. Municipal waste collected during the year [thousand t]	16, 54	22,18	14,23
3. Passenger cars per 1000 population [pcs.]	601,9	622,1	639,0
4. Public roads with hard surface (poviat and communal roads) per 100 km^2 [km]	251,0	251,0	246,2
5. Number of people with social benefits in total population [%]	2,3	2,2	2,2
6. Length of bicycle paths [km]	62,1	65,1	68,4

City/ Indicator	2018	2019	2020
Sopot			
1. Population density [person per km^2]	2086	2067	2042
2. Municipal waste collected during the year [thousand t]	19,04	18,14	16,96
3. Passenger cars per 1000 population [pcs.]	746,7	762,3	791,1
4. Public roads with hard surface (poviat and communal roads) per 100 km^2 [km]	54,2	56,9	57,1
5. Number of people with social benefits in total population [%]	3,4	3,3	3,9
6. Length of bicycle paths [km]	21,0	22,3	22,3

Source: own study based on GUS data

Table 2 shows the calculated values of partial and total utility for the examined cities with poviat rights.

Table 2. Values of partial and total utility for the cities examined

City / Indicator	2018	2019	2020
Gdańsk			
1. Population density- D	1	1	1
2. Municipal waste collected during the year- D	0	0,63	0.83
3. Passenger cars per 1000 population- S	0,31	0,34	0,31
4. Public roads with hard surface- S	0,24	0,25	0,27
5. Number of people with social benefits In total population - D	0,90	1	1
6. Length of bicycle paths -S	1	1	1
Total utility	**3,45**	**4,22**	**4,41**
Gdynia			
1. Population density– D	0,14	0,09	0,06
2. Municipal waste collected during the year- D	1	0	1
3. Passenger cars per 1000 population- S	0	0	0
4. Public roads with hard surface- S	1	1	1
5. Number of people with social benefits in total population– D	1	0,92	0,94
6. Length of bicycle paths - S	0,24	0,25	0,26
Total utility	3,38	2,26	3,26

City / Indicator	2018	2019	2020
Sopot			
1. Population density-D	0	0	0
2. Municipal waste collected during the year– D	0,12	1	0
3. Passenger cars per 1000 population- S	1	1	1
4. Public roads with hard surface- S	0	0	0
5. Number of people with social benefits in total population- D	0	0	0
6. Length of bicycle paths S	0	0	0
Total utility	**1,12**	**2**	**1**

Source: own study

The use of partial and total utility allows for easier interpretation of the values of sustainable development indicators in terms of the quality of life of the inhabitants of a given city. The analysis uses examples of indicators that directly affect the quality of life. Population density, environment, mobility and social assistance are selected areas of life that have a direct impact on the quality of life of residents.

3. Discussion

The years for which the most complete statistical data were available were selected for this analysis. The destimulants for the sustainable development of city areas in the Pomeranian voivodeship include: population density, waste generated during the year, the number of people with social benefits.

The research took into account 6 indicators, so the hypothetical maximum value of total utility is 6. The obtained results indicate that none of the cities examined reached the maximum value. There are large differences between the cities analyzed (1- 4.41). Highest Total Utility Value occurred in Gdańsk in 2020 (4.41). On the other hand, the lowest value of total utility between 2018 and 2020 was achieved by the city of Sopot, respectively: 1.12; 2; 1. For the remaining cities, the total utility values fluctuated in the following ranges:

- Gdańsk (3.45-4.41)
- Gdynia (2.26-3.38).

It is worth comparing the value of total utility to the value of pattern vector, i.e. the highest value that the city could achieve (the pattern vector is equal to the number of indicators examined). Graphically, the differences between individual cities and the value of pattern are presented in Figure 1.

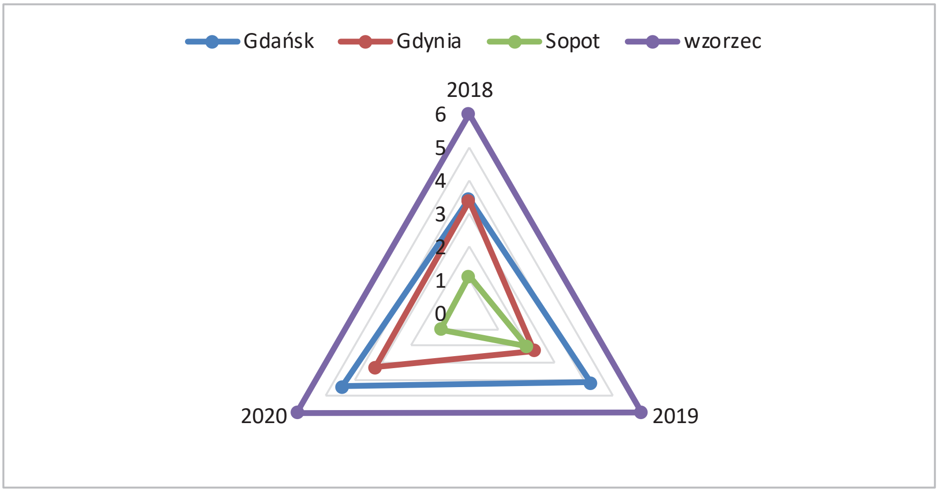

Fig. 1. The relation of the total utility value to the reference value for the cities analyzed between 2018 and 2020

Source: own study

Figure 1 shows quite large deviations from the pattern vector for the city of Sopot, where the value of partial utility was zero for the following indicators:
- density of population,
- public roads with hard surface (poviat and communal),
- number of people with social benefits,
- length of bicycle paths.

The city of Gdańsk is the closest to the benchmark value, where the value of 1 partial utility occurred for the following indicators:
- density of population,
- number of people with social benefits,
- length of bicycle paths.

Table 3 shows the percentage share of the total utility value to the benchmark value for the cities analyzed between 2018 and 2020.

Table 3. Percentage of the total utility value relative to the pattern for the cities examined

Cities	2018	2019	20202
Gdańsk	57,5%	70,3%	73,5%
Gdynia	56,3%	37,7%	54,3%
Sopot	18,7%	33,3%	16,7%

Source: own study

The paper assumes that the sustainable development in the cities examined, in terms of the objective quality of life, occurs when the mean total utility values exceed 50% of the reference value.

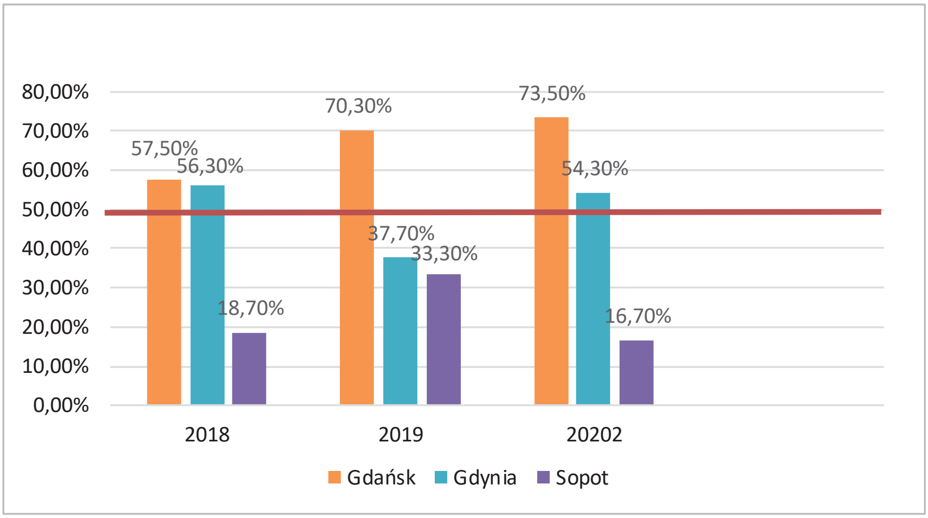

Fig. 2. Percentage of the total utility value in the pattern value for the cities analyzed between 2018 and 2020.

The above graph clearly shows the area of approximation or distance of the total utility value from the reference value. Values above 50% occur only for the city of Gdańsk in the entire time horizon analyzed. However, it is worth noting that also in Gdynia, the percentage of total utility in the benchmark value in 2018 and 2020 was also above 50%. The lowest percentages are noticeable for Sopot, where these values did not exceed 50% in any of the years analyzed.

Based on the research conducted, it can unequivo cally be stated that full balancing takes place only in Gdańsk.

It is worth paying attention to the scope of analyzes conducted on the basis of sustainable development indicators. The selection of indicators is often determined by the availability of data and the discretion of the authors. It is not always clear and obvious that data can be defined as stimulants or destimulants. In the indicators selected for this study, the determination of their positive or negative impact on the inhabitants' quality of life also remained subjective. The first indicator of population density clearly has an impact on the sustainability of cities. Cities are the source of wealth, but also the source of social, economic, spatial and environmental issues. Cities are favored by such development which provides them with jobs and tax revenues[18].

The demand for employment growth in the cities is accompanied by the increasing importance of aesthetic, climatic and lifestyle factors in the city. It is considered necessary to reduce the negative effects of urbanization and the use of chemicals that are hazardous to human health and the environment, e.g. by reducing waste generation, recycling it and using water and energy more efficiently[19].

Another waste-related indicator, from the point of view of the amounts collected, can also be a stimulus, showing the efficiency of waste management system. An indicator that can be used in research - the amount of illegal dumping sites removed could allow for an even deeper analysis. Waste, including municipal waste, is a macroeconomic issue - it is an integral part of the processes of production, consumption, investment, and thus the development and distribution of GDP. Waste

[18] Montgomery Ch., *Miasto szczęśliwe. Jak zmieniać nasze życie, zmieniając nasze miasta*, Wyd. Wysoki Zamek, Kraków 2015

[19] Wąsowicz K., Famielec S., Chełkowski M., Gospodarka odpadami komunalnymi we współczesnych miastach, Uniwersytet Ekonomiczny w Krakowie, 2018

occur throughout the economic and social life cycle - from the acquisition and consumption of renewable and non-renewable resources, consumption of other benefits of natural processes, and they are the source of resource waste. They arise inevitably, but their production can be limited by changing the awareness and style as well as the structure of consumption (counteracting and prevention)[20]. It is also worth paying attention to the aspect of maintaining the technical efficiency of the municipal waste management system, i.e. proper operation of municipal waste treatment facilities, as well as environmental monitoring of the pollutants potential emissions into the environment from these facilities. It should be pointed out that for the municipal waste incineration plants it is important to ensure the collection of generated heat and electricity, proper management of waste slag, fly dust and sludge from flue gas cleaning processes, as well as monitoring the emission of pollutants in flue gases[21].

Another indicator analyzed concerns the number of cars in use in the cities studied. The car, fulfilling the utility functions in passenger transport, satisfies the first-tier needs , and in the consumer society, when the quality of cars is diversified, its role is increasing as an object symbolizing the social status of owners, meeting the higher needs . In the social world of motorization, the car is a symbolic resource for car owners, a symbol of identification, and the criterion of belonging. It is difficult to find arguments justifying the sociologists' lack of interest in such a common component of everyday life as the car in the context of sociological studies of consumption, spatial mobility, mobility, interaction and urbanization[22],[23]. From this perspective, the number of cars should be treated as a stimulant indicating a factor of improving the quality of life. On the other hand, due to cars, city residents:

- live under conditions of road congestion and excess fumes and noise;
- bear the consequences of spatial segregation of particular user groups. The mass development of individual motorization has led to a vicious circle of

[20] Op. cit

[21] Szerzej: J. Famielec, S. Famielec, *Restrukturyzacja sektora gospodarki odpadami komunalnymi*, w: Restrukturyzacja sektorów gospodarki i przedsiębiorstw, red. J.

[22] D. Leśniak-Moczuk A. , *Społeczne funkcje samochodu w socjologii życia codziennego,*

[23] Urry John, Życie za kółkiem, [w:] *Socjologia codzienności*, red. Piotr Sztompka, Małgorzata Bogunia-Borowska, Wydawnictwo „Znak", Kraków 2008. 24

transport policy in modern cities. The more cities are adapted to the needs of passenger cars, the more the quality of life in these cities decreases, which is conducive to the migration of more and more residents to the sprawling suburbs. The supporters of the sustainable development transport policy propose to modify our lifestyle so as to maintain the achievements of civilization and not to lose the values of natural environment. A positive change in our lifestyle should be supported by the sustainable development transport policy and the rational management of urban mobility[24].

Another indicator analyzed concerns the length of roads, which should be considered a stimulant from the perspective of the quality of life. However, it is worth paying attention to the aspect of suburbanization. The spread of urban forms into rural areas is reflected in a different landscape, where, next to rural households, villas with small production and service establishments coexist. A kind of urban-rural continuum is most visible in metropolitan areas, where variability can be observed over large areas and the intensity of the management forms[25].

The indicator on the cycle path length should be considered a stimulus, but the spatial extent is critical at the design stage. The coherence of bicycle paths is of great importance and means that the routes connect all sources and destinations, allow (in a few minutes) easy access to them and allow you to choose travel options depending on your preferences; in densely built-up areas, the main routes should be supplemented with other lower-tier routes (collector or local roads). Failure to follow the main route or part of it could make the layout inconsistent, discontinuous and inaccessible, and may discourage the choice of a bicycle as a means of transport.

The last indicator concerns the social welfare in a broader sense, which from the perspective of the sustainable development principles, and thus improving the quality of life, is a stimulus. Therefore, social policy includes specific actions undertaken to promote welfare. At the center of sustainable development is a responsible and aware person who has knowledge, who creates social, economic and environmental

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[24] Wyszomirski O, *Zrównoważony rozwój transportu w miastach a jakość życia*, Transport miejski i regionalny 12 2017

[25] Raedo, R. *Urban sustainability deficits: The urban non-sustainability index (UNSI) as a tool for urban policy*. Sustainability 2021, 13,.

conditions for own development and the development of other people. Thus, the task of social policy in its active function is to generate such attitudes. Human social security, which is an element of sustainable development, cannot be achieved only through a system of benefits, allowances and subsidies. Active social policy consists in developing conditions and supporting individual and social activity[26]. In the study, this indicator was considered a destimulant, indicating the increase in the number of poor people who require social assistance, and social imbalance.

Conclusions

Based on the results of the analysis of the values of sustainable development indicators and the value of partial and total utility calculated on their basis for the studied cities, the following statements and final conclusions can be formulated:

1. The analysis of sustainability indicators is often related to the number of limitations; therefore, the use of total and partial utility allows to visualize these changes in a transparent and easy-to-interpret manner. This provides the possibility of using the above-mentioned tool by local authorities to implement corrective actions aimed to improve the inhabitants' quality of life. However, it is worth paying attention to defining indicators by aggregating them, defining positive or negative values.
2. Therefore, the essence of the selection of indicators is to indicate the sustainability or unsustainability of the development of Local Government Units. In this article, the indicators have been selected in such a way so that their increase or decrease (stimulant, destimulant) would not raise any doubts during the analysis.
3. As a result of applying the partial and total utility, the balance of the city of Gdańsk was indicated, while the lowest values of total utility for the city of Sopot indicate the lack of sustainability in this city and the need to implement corrective actions to stop this process.

[26] Nagórny W., *Polityka społeczna a zrównoważony rozwój*, Prace Naukowe AJD. Pragmata Tes Oikonomias 5, 137-146, 2011

4. The conducted research has shown that it is possible to apply the qualitative convention to assess the development changes of local government units. The calculated values of partial and total utility based on the values of sustainable development indicators turned out to be a good tool for assessing and comparing changes in the objective quality of life in the examined cities. Thus, it can be concluded that partial and total utility is used as a valuable supplement to the analysis of sustainable development indicators. This allows for a clear and more complete picture of the development of the cities studied, especially in relation to the reference vector.

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THE BALTIC SEA SPECIAL AREA UNDER MARPOL

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Abstract
Sea transportation can affect people's lives both positively, by supporting the economy, and negatively, by contributing to climate change and through pollution and accidents.
In spite of being economically cheap and environmentally friendly when measured in tons of transported goods, shipping also has negative effects on the environment. International Maritime Organization recognises that some areas need additional protection and MARPOL Convention defines certain areas as Special Areas (SA). These Special Areas are provided with a higher level of protection than other areas of the sea. The special area established under Annex V is the Baltic Sea Area.
The paper presents analysis of activities focused on environmentally friendly solutions as a form of IMO support for realization of the strategy of the Baltic Sea area protection.

Keywords: the Baltic Sea, environment, Special Areas

Introduction

Oceans cover approximately 71 percent of Earth's surface and hold 90 percent of planets' biomass. They are divided into several principal oceans and smaller seas. Because it is the core component of Earth's hydrosphere, the ocean is integral to all known life, forms part of the carbon cycle, and influences climate and weather patterns [Birnie &Boyle 2002].

Large ships have negative impacts on marine environment, wildlife and habitats trough accidental spills of oil, operational discharge of waste, chemical residues and water ballast. Ships produce a huge variety of solid and liquid wastes streams, including waste oil from the engine rooms, black water, grey water, dry waste, food and galley waste and others (Bicer & Dincer 2018, Mandic et al. 2021).

Shipping is an international industry and the regulatory framework must reflect this. The International Maritime Organization (IMO) is the United Nations specialized agency with responsibility for the safety and security of shipping and the prevention of marine pollution by ships. Its main role is to create a regulatory framework for the shipping industry that is fair and effective, universally adopted and implemented. IMO has developed rules to authorize coastal states to impose protective measures that restrict the freedom of navigation in ecologically sensitive marine areas [Letniewska 2020].

The International Convention for the Prevention of Pollution from ships is one in a number of Conventions adopted by the IMO to fulfil its remit. The main purposes of MARPOL Convention are to encourage the general adoption of the highest practicable standards in matters concerning maritime safety and control of marine pollution from ships. The objective of the Convention is to reduce the volumes of harmful materials entering the world's oceans and marine environment (Al-Enazi et. al 2021). It is considered to be the main international convention concerned with the prevention of marine environmental pollution caused by ships due to operational or accidental causes (Smith et al. 2020).

To achieve this goal, the Convention and its Annexes contain requirements to control the accidental or deliberate discharge of substances such as oil, chemicals and garbage. Waste oil is generated in a ship from several systems such as the sludge, slop, bilge, and ballast water system. Annex I (Regulations for the Prevention of Pollution from Oil) includes not only regulations relating to the construction of ships for the protection of marine environment but also a general prohibition on discharging oil into the sea.

Substances posing a threat of harm to the marine environment are divided into three categories: X, Y and Z. Category X substances are those posing the greatest threat to the marine environment. Annex II (Regulations for the Control of Pollution by Noxious Liquid Substances B in Bulk) deals with the transport of noxious liquid substances, which are conveyed in the form of bulk products, as well as discharging of liquid residues containing noxious liquid substances.

Annex III (Regulations for the Preventing of Pollution by Harmful Substances Carried by Sea in Packed Form) aims to identify marine pollutants using clear marks to distinguish them from other less harmful cargoes.

The discharge of raw sewage into sea can create a health hazard. Sewage can also lead to oxygen depletion and can cause an obvious visual pollution in coastal areas - a major problem for countries with tourist industries. Annex IV (Regulations for the Preventing of Pollution by Sewage from Ships) generally prohibits the discharge of sewage into sea with corresponding exceptions in accordance with its provisions.

The shipboard generated garbage is to be grouped into the following categories: plastics, food wastes, domestic wastes, cooking oil, operational wastes, cargo residues, animal carcasses and fishing gear. Garbage from ships can be just as deadly to marine life as oil or chemicals. The greatest danger comes from plastic which can float for years. Annex V (Regulations for the Preventing of Pollution by Garbage from Ships) contains provisions intended to prevent pollution by garbage from ships, with different requirements in accordance with the type of garbage to be disposed of.

Annex VI (Regulations for the Preventing of Air Pollution from Ships) intends to limit air pollution from ships. It affects ozone-depleting substances (ODS), nitrogen oxides (NOx), sulphur oxides (SOx), and particulate matter (PM) volatile organic compounds (VOCc), shipboard incineration, reception facilities, fuel oil quality, energy efficiency design of ships, and ship energy efficiency management plan (SEEMP).

The MARPOL Convention defines certain areas as "Special Areas" in which *for recognized technical reasons relating to their oceanographical and ecological condition, and to their particular character of its traffic, the adoption of special mandatory methods for the prevention of sea pollution by oil, noxious liquid substances, or garbage, as applicable, is required.* Special Areas are defined in terms of the pollution types covered in each of the Annexes to MARPOL (Annex I – oil, Annex II – noxious liquid substances, Annex V – garbage). Under MARPOL Annex VI, such areas are called Emission Control Areas. They are designated by IMO's Marine

Environment Protection Committee and include: the Mediterranean Sea area, Baltic Sea area, Black Sea area, Red Sea area, Gulfs area, Gulf of Aden, Antarctic area, North Sea, Wider Caribbean, North West European waters.

Under the Convention, these Special Areas are provided with a higher level of protection than other areas of the sea. Any discharge into the sea of oil or oily mixture from the cargo area of an oil tanker shall be prohibited while in a special area. The discharge of sewage from passenger ships within a special area is generally prohibited. Annex V of the Convention prohibits the disposal of plastics anywhere into the sea and severely restricts discharges of other garbage from ships into coastal waters and Special Areas.

In 1990, IMO (through its Marine Environment and Protection Committee) adopted regulations to protect the marine environment by identifying Special Areas of protection - A Particularly Sensitive Sea Areas (PSSA). They are areas that need special protection through action by IMO because of their significance for recognized ecological, socio-economic or scientific reasons and which may be vulnerable to damage by international maritime activities. The Great Barrier Reef, which had long been considered an area of ecological, social, cultural, economic, and scientific importance, was recognized as the first PSSA. To give an area the status of a PSSA is potentially a very important designation for the protection of that area (Lefebvre-Chalain 2007).

The PSSA mechanism offers several benefits. It provides a comprehensive tool for evaluating and managing marine risks. Specific associated protective measures can be used to control maritime activities in that area, such as compulsory pilotage programs, separate shipping, traffic lanes, areas to be avoided, reporting requirements, no anchor zones, strict application of discharge and equipment requirements for ships, and installation of vessel traffic services (Roberts 2007).

A total of 13 areas have been designated as PSSAs by the International Maritime Organization worldwide.

The criteria to allow areas to be designated as Particularly Sensitive Sea Area are presented in Figure 1.

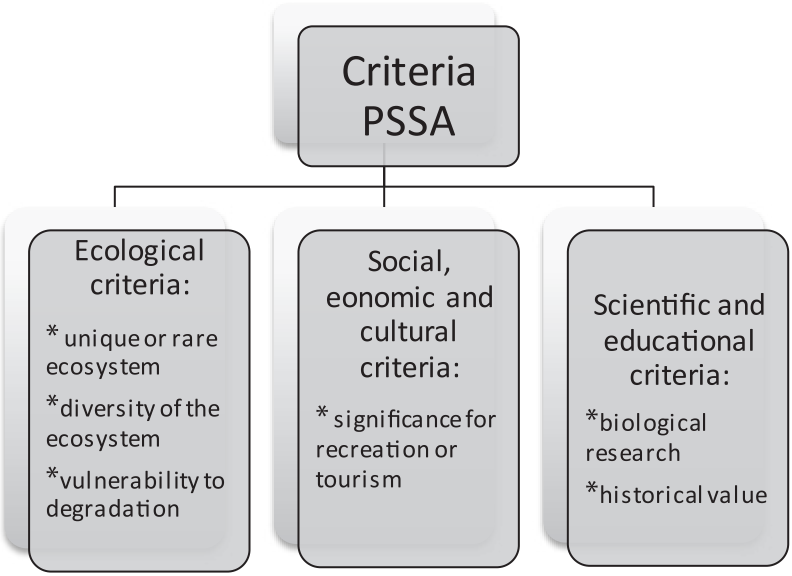

Fig. 1. The criteria for the identification of particularly sensitive sea areas.

Source: [own study].

The criteria for the identification of PSSA and criteria for the designation of Special Areas are not mutually exclusive (IMO 2006). To be identified as a PSSA, area must meet at least one of the ecological, socio-economic or scientific criteria. In many cases, a Particularly Sensitive Area may be identified within Special Areas.

Many specific IMO measures can be used to control the international shipping activities in PSSAs such as routing measures, strict application of MARPOL discharge and equipment requirements for ships, such as oil tankers, and Vessel Traffic Services.

The paper presents analysis of activities focused on environmentally friendly solutions as a form of IMO support for realization of the strategy of the Baltic Sea area protection.

1. Baltic Sea Area

The Baltic Sea is one of the largest brackish water areas – or of low salinity – in the world, with a surface area of 420,000 km^2. The water catchment area of the Baltic Sea is about four times larger than its surface area and is inhabited by around 85 million people. Geologically, the Baltic Sea is very young. Most of the species of marine origin in the Baltic Sea originate from a time when the sea was saltier, and since then they have had limited genetic exchange with their counterparts in fully marine waters. Connected with the Atlantic Ocean only via the Kattegat, a shallow strait, complete water exchange in the Baltic takes around 30 years (Leppäranta & Myrberg 2009). Due to its enclosed nature and relatively low biodiversity, the Baltic Sea is especially vulnerable to environmental pressures. Figure 1 presents typical pressures occurring in sea the Baltic Sea

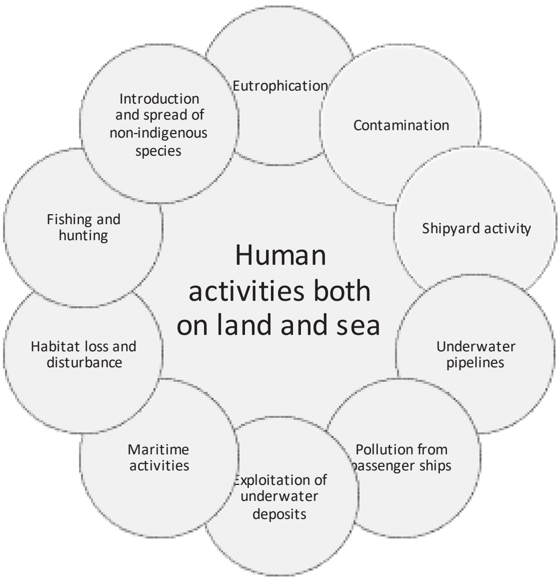

Fig. 2. Human activities influence on the condition of the Baltic Sea area

Source: [own study].

The Baltic region is currently one of the most dynamic regions in the world. The Baltic Sea has some of the busiest shipping routes in the world. Around 2000 sizeable ships are normally at sea any time in the Baltic. More than 9% of the global maritime volumes and 117 million ferry passengers passed the Baltic Sea ports and the cruise ship tourism has expanded (Wilewska-Bien & Anderberg 2018). Marine traffic in the Baltic Sea is in constant growth. The recent rise in shipping activities in the area may be linked to the economic expansion of the Baltic Sea countries.

The Baltic Sea has often been called the most polluted sea in the world (Leppärant & Myrberg 2009). With increasing population, industrialization, and intensification of agriculture, the pressures on the sea increased dramatically (Ollikainen et al. 2019).

Maritime transportation is potentially an environmentally friendly way of transporting goods and passengers, but current practices include extensive emissions of nitrogen oxides (NOx), sulphur oxides (SOx) and particulate matter (PM). Discharges to the Baltic Sea water include accidental large oil spills but also small continuous leakages, release of wastewater, use of antifouling paints, exchange of ballast water containing potential invasive species and other littering. In order to become a cleaner mode of transport, maritime shipping has to considerably reduce its emissions of air pollutants and to develop systems for firm control of illegal discharges of sludge and other types of waste (Kågeson 2010).

Nutrients, especially Nitrogen (N) and Phosphorous (P) from sewage discharged into the sea from passenger ships contribute to the problem of eutrophication where excessive growth of algae, plankton and other microorganisms can have serious negative effects on other organisms like fish, birds and even people. Due to semi-enclosed nature of the Baltic Sea, it is very susceptible to eutrophication. The main contributor to the eutrophication problem is land-based runoff, however, sewage from passenger ships due to the number of persons on board is also a contributing factor. It is estimated that one person on a cruise ship generates between 20÷40 dm^3 of sewage and 120÷300 dm^3 of grey water daily. The discharge of untreated wastewater into sea can spread pathogens to the marine environment and contribute to nutrient and oxygen depletion.

The Baltic Sea ecosystem is protected by several complex mechanisms, including IMO and other UN instruments:

- global conventions: The International Convention for the Prevention of Marine Pollution from Ships (MARPOL 73/78), The International Convention on the Control of Harmful Anti-Fouling Systems on Ships, and International Convention for the Control and Management of Ship's Ballast Water and Sediments, The United Nations Convention on the Law of the Sea (UNCLOS);
- regional conventions, regulations and initiatives: the Convention on the Protection of the Marine Environment of the Baltic Sea Area (Helsinki Convention), European Council Directive 92/43/EEC on the conservation of the natural habitats and of wild fauna and flora, Declaration on the Safety of Navigation and Emergency Capacity in the Baltic Sea Area
- national legislations and regulations adopted by the nine Baltic Sea countries,

The United Nations Convention on the Law of the SEA provides a universal legal framework for the management of marine resources and their conservation. Navigation rights, territorial sea limits, economic jurisdiction, legal status of resources on the seabed beyond the limits of national jurisdiction, conservation and management of living marine resources and protection of the marine environment are among the features of the treaty.

The Helsinki Convention entered into force on 3 May 1980. For the first time ever, all the sources of pollution around an entire sea were made subject to a single convention. The Convention covers the whole of the Baltic Sea area, including inland waters as well as the water of the sea itself and the sea-beds.

The Baltic Sea area has been designated as a Special Area under Annexes I, II IV and V of MARPOL Convention. The Baltic Sea area PSSA was created by IMO Resolution MEPC in 2005, which means special measures are required for vessels operating in the Baltic Sea.

1.1. Policy instruments for reduction of emissions from ships

Shipping activities contribute significantly to the air pollution in the Baltic Sea region. Emissions of SO_x from shipping due to combustion of marine fuels with high sulphur content contribute to air pollution in the form of sulphur dioxide and particulate matters, harming the environment and human health, the latter particularly around coastal areas and ports.

NO_x emissions from ships cause acid depositions that can be detrimental to the natural environment and also contribute to eutrophication. Shipping is among the largest contributors of NO_x deposition to the Baltic Sea. NO_x also contribute to the formation of ground level ozone which is a major health hazard as well as a very important greenhouse gas.

Various market-based approaches share advantages relative to the less flexible regulatory approaches, such as a requirement that every ship achieve the same emission rate or install the same equipment.

Under the MARPOL Convention, the rules which seek to reduce NO_X and SO_X were adopted and emission control areas were established.

SOx controls apply to all fuel combustion equipment and devices on-board of ships. The SOx emission control areas (ECA) are: the Baltic Sea, the North Sea, the North American Area and United States Caribbean Sea Areas. The regulation limits the maximum sulphur content of the fuel used and has two stringency levels: one stringency level that holds in SO_x emission control areas and, another less stringent level for outside ECAs as a global requirement.

Ships trading in designated emission control areas have to use fuel oil with a sulphur content of no more than 0,1% from 1 January 2015.

As a consequence of the new regulation, ships have started to use low sulphur fuel oil. An increasing number of ships use as gas a fuel or fuel with low flashpoint. The severe limits concerning the sulphur content of marine fuels will definitely increase the cost of shipping. The derivative effects of the changes could result in a limitation of the competitiveness of the Polish and European economy.

Annex VI of MARPOL Convention introduces a stepwise approach to the reduction of emission of NO_x. Regulation of MARPOL sets NOx emission limits for installed marine diesel engines. The IMO emissions standards are commonly referred to as Tier I, II and III. The Tier I standards were defined in the 1993 version of Annex VI, while Tier II and III standards were introduced as Annex VI amendments adopted in 2008. Currently, no specific stringency levels hold for NOx emission control areas, but ships constructed on or after 1 January 2016 have to comply with specific standards when operated in the North American ECA or the United States Caribbean Sea ECA.

The control of engine NO_X emission is achieved through the survey and certification requirements leading to the issue of an Engine International Air Pollution Preventing Certificate. Different levels of control apply based on the ship construction data and engine's rated speed.

1.2. Other marine environmental protection solutions

Operational discharges of oil have been severely restricted in the Baltic Sea since 1983 (Annex I). Discharges from the machinery spaces of ships of 400 gross tonnage and above are permitted, provided that the content of oil in the effluents does not exceed 15 parts per million. In spite of these restrictions, illegal discharges from ships are frequently being detected. Considering growing trends in ship traffic in the region, a decrease in the number of illegal oil discharges reflects a positive trend (EMSA 2012).

The discharge of garbage from ships in the Baltic Sea has been prohibited since 1988 (Annex V). Plastics, including synthetic ropes and synthetic fishing nets, plastic garbage bags and incinerator ashes from plastic products, which may contain toxic or heavy metal residue, paper products, rags glass, metal, bottles, crockery, dunnage, lining, packing materials and other garbage may not be disposed in the Baltic Sea waters. In spite of the restriction, the overall problem of garbage can be commonly observed in the Baltic Sea and along the shoreline. Because garbage in the sea may be originating from both land-based and ship sources, it is difficult to evaluate the contribution from shipping activities (HELCOM 2013).

In 2011, the International Maritime Organization has designated the Baltic Sea as a Special Area with stricter sewage discharge requirements for passenger ships under MARPOL Convention (Annex IV). The shipping industry has been progressively regulated to reduce the risk of pollution by sewage from ships occurring. The number and severity of sewage pollution accidents are minimal to zero and the number of discharge incidents are minimal depending on the type of ship and its flag state. Pollution incidents do, of course, occur but are now infrequent and are often on a minor scale.

Passenger ships not equipped with an on-board sewage treatment facility according to the specification will have to discharge the sewage in port area. There is requirement that ports and terminals in the Baltic Sea area must provide adequate facilities for the reception of sewage being discharged from passenger ships. First, the ban on the discharge of sewage was to be introduced in 2016 for new passenger ships and in 2018 for existing passenger ships, but these dates have been postponed until 2019 due to insufficient port reception capacity in the region (MEPC 2016). The new regulations took effect for all passenger ships on 1 June 2021. There are several challenges in the process of expanding of the reception capacity. Ports are at the interface between the areas regulated by international maritime regulations and the different rules and regulations on land. The offloaded ship wastes have to be processed further on shore which involves other actors than ports. Agreements between ports and municipal sewage treatment plants are therefore necessary.

2. Discussion

For a long while, many people believed that the oceans could absorb anything that was thrown into them, but this attitude has changed along with greater awareness of the environment. In order to prevent economic growth from having adverse effect on the natural environment, further measures to reduce emissions from shipping are urgently needed.

The effectiveness of the special protection of Baltic Sea through action by IMO is discussed by scientists and maritime experts. The most frequently mentioned gap was that key requirements are not sufficiently monitored in space (Kahler et al. 2020).

The definition and coverage of PSSAs have been expanded to better protect the marine environment and to readjust the balance between the freedom of navigation and interests of the coastal state. At the time of the creation of the PSSA, the Baltic Sea was experiencing some of the densest maritime traffic in the world with more than 2,000 ships—including 200 oil tankers—estimated to be route on an average day. The intensity of traffic together with meteorological and oceanographic factors considerably increases the risk of accidents and pollution. The creation of the PSSA in the Baltic Sea was driven mainly by ecological factors, which carry, nonetheless, economic, social, cultural, scientific and educational considerations. The PSSA sought primarily to reduce the risk of accidental pollution from ships and thereby protect the Baltic Sea habitats and species. Essential factors in achieving the goals of the Baltic Sea protection are regional support and efficient cooperation among neighbouring countries. No accidents have been registered on the waters of the Baltic Sea since the creation of the PSSA. However, several minor illegal oil discharges have been recorded in recent years. Therefore, it can be stated that the protection status of these areas could be improved through enhanced monitoring and spill response preparedness.

Management of sewage from ships because of regulations is naturally in focus in the Baltic Sea region. Waste handling in compliance with international and local regulations needs to be easy for the crew with clear procedures for sorting and separating the waste and user-friendly solutions for reducing its volume on board. Much education and training is undertaken on these aspects internationally and locally, as well as part of on board training and procedures incorporated in safety management systems on ships.

Despite the fact that discharge of garbage from ships in the Baltic Sea has been prohibited since 1988, the overall problem of marine litter such as plastic products, glass, bottles, packaging material is observed in the Baltic Sea waters (Veneeckhaute & Fazli, 2020). Because garbage in the sea may originate from land and ship sources it is difficult to evaluate the contribution from ships activities. Creation of national monitoring in place for marine litter seems necessary. In order to ensure that officers and crew are fully aware of the obligations of Annex V, a good solution would be to prepare and issue a garbage management manual.

Annex VI to MARPOL obliged manufacturers and shipping companies to follow the rules in ship design and manufacturing considering the air pollution from ships. The maximum allowable fuel Sulphur content for shipping in the Baltic Sea dropped from 1 % to 0,1 % on 1 January 2015. MARPOL Annex VI regulations on Sulphur in ships fuel causes additional cost for the sea transport. Rational energy use is the key issue for the shipping industry due to increasing bunker cost (Cullinane & Bergvist 2014).

The implementation of sulphur regulations requires positive benefits, meaning that the benefits must outweigh the cost (Jiang et al. 2014). The European Commission authorized a cost-benefit analysis to study the impact of Annex VI. The study indicates positive net benefits for the Baltic Sea. The resulting health benefits are up to 5 billion Euro, while the corresponding cost for the sea transport is in the range of 170÷900 million Euro (Antturi et al. 2016.)

One of the possible measures for mitigation of the environmental impact could be switching to environmentally friendly fuel that is more acceptable for the environment. Currently, there are some another options for sulphur removal. The first option is to continue to operate on high sulphur fuel and install sulphur scrubbers, the second one is to switch to marine gas oil. The cheapest and the quickest way to reduce fuel consumption is to travel at lower speed (Doudnikoff & Lacoste 2014).

3. Conclusions

Shipping is an essential component of any programme for further sustainable economic growth. It is powerful sector of the global economy making a major contribution to global trade and prosperity and has a relatively negative impact on the environment. It is also worth considering reducing or stopping the growth of consumption and the volume of freight transport in accordance with the principle of sustainable development.

The expected economic development in the Baltic region, in which about 80 million people now live has positive as well as negative aspects for the environment. The protective measures brought have already led to improvements to the ecological situation in the Baltic Sea.

IMO regulations concerning the protection of the Baltic Sea represent a challenge not only for the maritime industry, but also for the ports of the Baltic Sea region. The requirements of the Special Area and PSSA have resulted in several environmental improvements such as reduction in air pollution, limiting of the discharge of garbage and sewage, decrease in maritime incidents and oil spills as well as cumulative effects of the above. Furthermore, improving maritime environmental standards in the Baltic Sea may be achieved using national regulations. Such actions could include improvements to the satellite-based detection services for oil spills and polluting vessels, as well as to response resources. Another recommendation would be to provide economic incentives for shipping companies operating in accordance with the environmental standards.

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ANALYTICAL CHALLENGES OF DETECTION AND DETERMINATION OF NANO- AND MICROPLASTICS IN FOOD AND ENVIRONMENT

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Abstract
The pollution caused by micro- and nanoplastics in food products and different environmental samples is regarded as one of the most serious environmental issues worldwide. This is mainly due to their slow degradability, biological ingestion by aquatic living organisms, and consequently acting as carriers to accumulation as well as transport synthetic organic pollutants. Moreover microplastics and chemical additives added to plastics during manufacture process can enter food chains and potentially cause humans serious health problems. There is no legislation for micro- and nano microplastics as contaminants in food and other elements of the environment. It is fundamental to draw greater attention to assessments of the effect of accumulation of nano- and microplastics in various environmental samples. To date, literature data on this subject are very limited.
In order to estimate the amounts of different kinds of micro- and nanoplastics in food products and various elements of the environment, appropriate analytical methodologies are required. The methodologies designed to determine micro- and nanomicroplastics in samples of food and environment can be used to track the environmental fates of these pollutants, i.e. the transport, the chemical, biological and photochemical transformations these compounds.

Keywords: microplastics, nanoplastics, food pollution, food quality management, environmental quality management, sustainable development

Introduction

Due to their durable, lightweight, strong, corrosion-resistant, low thermal and electrical conductivity plastics have become universal materials in packing, transport, building and construction sectors [Dümichen et al. 2017; Lechner et al. 2014; Meng, Kelly, and Wright 2020]. Synthetic polymers were first developed in 1907, but mass production of plastic have been started since the 1940s and 1950s [Meng et al. 2020; Thompson et al. 2009]. At that time, the level of plastic production was less than one million tons annually worldwide. However, since then there is a noticeable trend of ever-increasing both the production and the application of plastics [Meng et al. 2020]. For example, in 2014, global plastic production reached 311 million tons. While, in 2016, polymeric production was already at the level of 335 million tonnes worldwide and it is projected to rise further [Dümichen et al. 2017; Meng et al. 2020; Wirnkor et al. 2019]. Due to improper waste disposal, a significant part of this production volume can reach the environment. Plastic debris is accumulating in both aquatic and terrestrial systems globally [Meng et al. 2020].

The degradation process of plastics is very slow and polymers may be broken down into microplastics or even nanoplastics under the long-term action of oxidizing atmosphere, sunlight or other chemical, physical and biological factors [Andrady 2011, 2015; Yu, Zhou, and Li 2019]. As a new persistent environmental contaminant, microplastic pollution has attracted great interest recently [Yu et al. 2019].

Based on the available literature data it can be concluded that nano- and microplastics is ubiquitous in the environment (world's oceans, lakes, rivers, terrestrial and aquatic animals) [Dümichen et al. 2017]. Nowadays, microplastic penetration into the environment constitute a serious environmental problem.

As a consequence the presence of nano- and microplastics has been frequently detected in consumed by humans food, especially in fish and seafood [Cózar et al. 2017; Śmiechowska 2018; Woodall et al. 2014]. Therefore, it is essential to monitor concentration of micro- and nanoplastics in food and other elements of the environment, measure their levels of toxicity and assessments of the effect of accumulation of nano- and microplastics on a continuous basis. The authors' intention is to present a critical review of literature data concerning:

- Categorizations, sources, occurrence, transport and of nano- and microplastics;
- Impact on the environment and food safety;
- The analytical methods available for determining nano- and microplastics;
- Problems and challenges posed by analysis of nano- and microplastics.

1. Categorizations, nano- and microplastics sources, occurrence and transport

Degradation of larger plastic debris (macroplastic) leads to the formation of small polymer particles called microplastics [Andrady 2015]. Microplastics may be defined as a very heterogeneous mixture of diversely shaped polymer particles referred to as fibres, fragments, spheroids, pellets, granules, flakes or beads in the range of 0.1–5,000 μm [Petersen 2016]. In turn, nanoplastics may be defined as a polymer particles with any external dimension in the nanoscale or having surface structure or internal structure in the nanoscale (0.001–0.1 μm). Generally, there is no internationally recognised definition of microplastics and some authors have suggested also other categorizations [Petersen 2016; Pinto 2018; Wirnkor et al. 2019].

Generally, there are different types of polymers, but only a few are primarily reported in microplastic investigations: polystyrene (PS), polypropylene (PP); high-density polyethylene (HD-PE), low-density polyethylene (LD-PE), polyethylene terephthalate (PET), polyamide (PA), poly(vinyl chloride) (PVC) and nylon [Dümichen et al. 2017; Valeria Hidalgo-Ruz, Lars Gutow, Richard C. Thompson 2012]. A complete understanding of nano- and microplastics origin, transport processes, fate of plastic debris is essential in order to more complete quantify plastic pollution in global terms and to substantial reduce sources of emission [Emmerik 2020].

The micro- and nanoplastics can be introduced directly into the water, sediments already as micro- or nano-sized particles (primary micro-and nanoplastics). On the other hand, the micro- and nanoplastics present in aquatic systems result from the fragmentation of larger plastic debris (secondary micro-and nanoplastics) [Gabriel et al. 2018; Petersen 2016]. The origins of micro- and nanoplastic in environment might be attributed to the following sources: cleaning and cosmetic products (e.g. exfoliating creams, toothpastes, scrubs); 3D printing; fishing gear; packages and drink bottles; car tyres; textile fibers (washing, drying cycles); industrial feedstocks (manufacture of plastic goods); plastic resins (air blasting); cigarette filters; electronic equipment and paints [Andrady 2015; Gabriel et al. 2018; Pinto 2018].

The occurrence of microplastics especially in marine waters is relatively widely documented [Ravit et al. 2017]. Microplastics contamination is also noticeable in freshwater systems at concentration level higher than those reported in the world's oceans [Ravit et al. 2017]. Micro-and nanoplastics entering aquatic systems mainly through household sewage discharge and urban runoff [Jiang 2017]. Wastewater treatment plants (WWTPs) were not designed to remove this kind of contaminants during treatment [Ravit et al. 2017]. Urban rivers can be a significant component of micro- and nanoplastic transport, contributing to the global nano- and microplastic lifecycle [Ravit et al. 2017]. Furthermore, atmospheric transport has to be considered as a route of microplastic pollution [Petersen 2016]. Microplastics have been detected in fish (e.g., 2.1 particles/fish-mesopelagic, size: > 10,000 μm), vertebrates (e.g., 0.75 particles/g wet weight of brown shrimp, size: 200–1,000 μm), zooplanktonic organisms, terrestrial animals and other human food (e.g., beer- 0.033 fragments/mL), food ingredients (salt- 0.550–0.681particles/g; honey- 0.166 fibres/g, size: 40–9,000 μm) and drinking water [Petersen 2016]. For example, among the 25 commercially important fish species contributing mostly to global sea fishing, 11 were found to contain microplastics [Dümichen et al. 2017]. Considering the literature data, it can be concluded that microplastics have the high potential to transfer into human food chains [Dümichen et al. 2017; Gabriel et al. 2018; Petersen 2016; Śmiechowska 2018].

2. Impact on the environment and food safety

Nano- and microplastics are resistant to degradation in the environment and have the ability to accumulate in various ecosystems [Gabriel et al. 2018]. Therefore, nano- and microplastics are considered as an emerging problem of great concern [Gabriel et al. 2018]. Recent studies have shown different effects on marine animals due to exposure to microplastics, inter alia, mortality, reduced body mass, feeding rate, metabolic rate, reduced allocation of energy for growth, reduced swimming performance, changes in behavioural responses, decreased predatory performance, neurotoxicity caused by acetylcholinesterase inhibition, oxidative stress and intestinal damage [A.C.Welden and R.Cowie 2016; Gabriel et al. 2018; Gray D. Austin and Weinstein John E. 2017]. Moreover, microplastics can contain additives (ca. 4%) and the microplastics can adsorb contaminants such as toxic metals, styrene, bisphenol A (BPA), phthalates, polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCB) [Gabriel et al. 2018; Petersen 2016; Śmiechowska 2018]. In turn, different types of chemical products used during plastic manufacturing are also very toxic to humans and animals (e.g. neurotoxic, chemicals carcinogens, endocrine disruptors) [Gabriel et al. 2018; Meng et al. 2020; Wright and Kelly 2017]. Knowledge about the effects of nano- and microplastics indicates on potentially adverse consequences for environmental health, ecosystem services, biodiversity conservation and human food security and health. Nevertheless, this research topic is not yet fully understood and requires further investigation. At this stage, particularly important is properly assess, manage the risks, perform more laboratory research on the effects of nano- and microplastics, especially in terms of the long-term effects [Gabriel et al. 2018].

3. The analytical methods for determining nano- and microplastics

Due to the possible negative impact on the environment, human food security and health, qualitative and quantitative monitoring of micro- and nanoplastics is essential [Dümichen et al. 2017].

Until now several procedures have been developed for analysis polymers. Visual examination of the isolated microplastics is most often carry out in every test to separate and distinguish microplastics from other materials. This step is performed with using a microscope or by the naked eye [Petersen 2016]. Categories applied to describe microplastics including few factors such as source, erosion, shape and colour. Dissecting microscopes, stereo microscopes, visual-assisted microscopy or scanning electron microscopic methods have been used in this kind of study [Petersen 2016]. For analysis, non-destructive imaging techniques like Fourier-transform infrared spectroscopy (FTIR) and RAMAN imaging have been preferred. These analytical methods are capable to identify polymer at resolution in the range from ca. 10 μm (IR) to 0.5 μm (RAMAN) [Dümichen et al. 2017; Jiang 2017; Petersen 2016]. Main disadvantages of above mentioned techniques are the time consuming scanning procedure and uncertain extrapolation. Therefore, these techniques are difficult to apply as routine analysis. Microplastics were also analysed by using pyrolysis coupled to gas chromatography with mass spectrometry (Py-GC-MS). This technique is dedicated for samples weighing from 0.1-0.5 mg and works properly for single particles. Nevertheless, this method is susceptible to contaminants and also it is time consuming [Dümichen et al. 2017; Jiang 2017; Petersen 2016]. Other technique used for identify and quantify microplastics in different kind of samples is combination of thermal extraction with thermogravimetric analysis (TGA) on solid-phase adsorbers and subsequent analysis the absorbers by using thermal desorption coupled with gas chromatography with mass spectrometry (TDS-GC-MS). The use of this analytical method enables the fast identification and quantification of compounds with high molecular mass, specific organic decomposition products at very low concentration level. Disadvantage of this method is the lack of information about size distribution of polymeric particles [Dümichen et al. 2017].

Among all characterization methods it is crucial to develop efficient, accurate and reproducible procedures for collection of samples and separation of nano- and microplastics. Furthermore, it is necessary to develop standardized validation protocols for determination of nano- and microplastics [Jiang 2017].

4. Problems and challenges posed by analysis of nano- and microplastics

The analysis of micro- and even nanoplastics is faced with new challenges, especially the necessity to determine an analytes in samples with a very complex (and sometimes variable) matrix composition. The development of analytical techniques is necessary for ecotoxicological reasons and the requirement to improve the accuracy of descriptions of the state of the environment, human food security and health.

To date, few data have been published on the results of analyses of microplastics in various environmental samples and food products [Dümichen et al. 2017; Emmerik 2020; Meng et al. 2020; Müller et al. 2020; Ravit et al. 2017; Wirnkor et al. 2019; Yu et al. 2019]. Nevertheless, without an assured level of control and quality of results, the reliability of analytical information that one wishes to acquire on the basis of measurement data sets must be called into question.

Regardless of where and the extent to which micro- and nanoplastics are investigated, this is a very great analytical challenge. The most important problems to be solved and obstacles are presented in Fig. 1. These significant gaps in the current knowledge requires recognition and detailed completion.

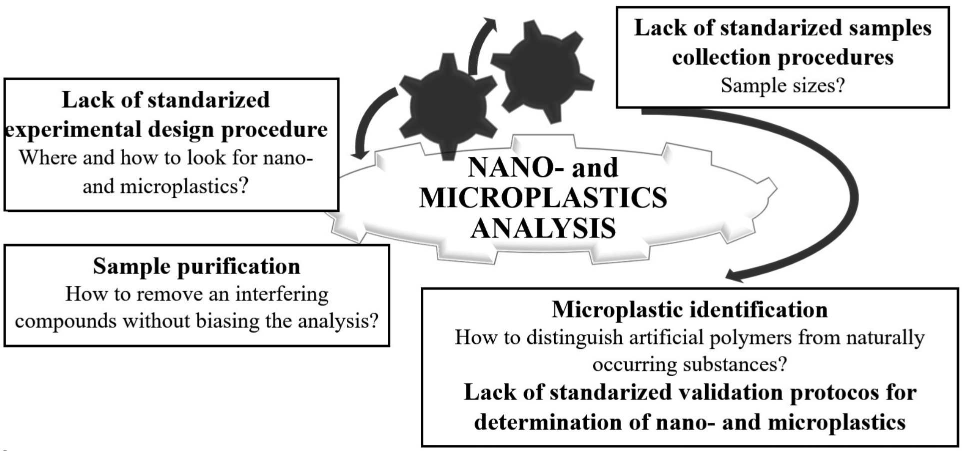

Fig.1. Problems and challenges posed by analysis of nano- and microplastics

CONCLUSION

This brief review highlights the ubiquity of microplastics in the environment, which can be associated with high potential of transfer of nano- and microplastics into human food chains. There are a large number of sources of nano- and microplastics in the environment. Preliminary study results on nano– and microplastic pollution demonstrated their potential negative effects for environmental health, toxicity and bioaccumulation ability. Although results of microplastics research have been relatively widely documented, collecting information is constantly incomplete, fragmented and biased. Basis on date base on presence of microplastics in various environmental samples and food products, current knowledge of its occurrence, sources, transport, fate, potential impacts and eventual solutions remain in its infancy [Meng et al. 2020]. It is crucial and urgent to expand the range of nano- and microplastics research. The current analytical methods are size restrictive and laborious. In case of nanoplastics in food, no analytical methods exist for identification and quantification these kind of contaminants. It is necessary to develop more sensitive, reliable and time-efficient analytical procedures for monitoring nano- and microplastics in the environment samples and food products. Besides, more groundwater study in the field of monitoring of nano- and microplastics in drinking water is needed. The sampling techniques also should be improved, because representative nano- and microplastic samples are decisive for accurate analyses and subsequent interpretation. The risk assessment of nano- and microplastics is still in its infancy. Therefore, future research is required to obtain qualitative and quantitative data to in-depth understanding the scale of the problem. The detailed research results on this scientific topic may constitute a valuable database for managing the quality of the environment and preventing the introduction of these pollutants into the environment, thus reducing the negative impact on food security and subsequently quality of life.

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ANALITYCZNE WYZWANIA DETEKCJI I OZNACZANIA NANO- I MIKROPLASTIKÓW W ŻYWNOŚCI I ŚRODOWISKU

Streszczenie

Zanieczyszczenie żywności oraz różnych elementów środowiska mikro oraz nanoplastikami budzi coraz większy niepokój, co wiąże się z bardzo wolnym procesem degradacji tego typu zanieczyszczeń w środowisku oraz spożywaniem nano i mikroplastików przez ryby oraz inne organizmy wodne. Ponadto nano- mikroplastiki mają znaczną zdolność do kumulacji w tych organizmach. Co więcej barwniki, które dodawane są do plastików w trakcie procesu produkcyjnego również mogą trafiać do łańcucha pokarmowego. Sumarycznie wszystkie te zanieczyszczenia mogą powodować poważne problemy zdrowotne. Stwarza to duże zagrożenie dla jakości i bezpieczeństwa żywności pochodzącej z akwenów wodnych, bowiem obecnie nie ma norm dotyczących dopuszczalnych poziomów zawartości mikroplastików w żywności i poszczególnych elementach środowiska.

Konieczne jest więc zwrócenie większej uwagi na ocenę stopnia akumulacji nano i mikrolpastików w produktach spożywczych oraz poszczególnych elementach środowiska. Jak dotąd liczba danych literaturowych na ten temat jest bardzo ograniczona.
W celu określenia w jakim stopniu zagrożone są poszczególne elementy środowiska oraz produkty żywnościowe nano i mikroplastikami, niezbędne jest opracowanie odpowiednich procedur analitycznych w celu identyfikacji oraz ilościowego oznaczenia tego typu zanieczyszczeń. W pracy zostaną przedstawione problemy związane z opracowaniem metodyki oznaczania nano- i mikroplastików w próbkach żywności oraz wybranych elementach środowiska. Posiadanie odpowiedniej metodyki badań pozwoli śledzić „los środowiskowy" tych związków chemicznych, ich przemiany chemiczne, fotochemiczne i biologiczne.

Słowa kluczowe: mikroplastiki, nanoplastiki, zanieczyszczenia żywności, zarządzanie jakością żywności i środowiska, zrównoważony rozwój

APPLICATION OF VOLTAMMETRIC DNA BIOSENSOR BASED ON SCREEN-PRINTED CARBON ELECTRODES FOR THE DETECTION OF COPPER IN DRINKING WATER

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Abstract
Heavy metals are one of the most dangerous pollutants due to their serious threat to the environment and human health. Among them, much attention has been devoted to copper (II) ions. Positively charged copper (II) cations can be detected using electrochemical DNA sensors. The work presents a comparison of chosen screen-printed carbon electrodes (SPCEs) and carbon paste electrode (CPE) as inexpensive and usable elements in electrochemical sensors. All electrodes were examined in terms of their sensitivity, potential working range, redox reaction reversibility, surface roughness, and double-layer capacitance. The sensor response was compared with the copper concentrations measured by the atomic absorption spectrometry method. The constructed sensor can be used as a portable handheld device to control real samples of drinking, spring, or other types of water.

Keywords: electrochemical DNA biosensor, copper detection, screen-printed electrodes, carbon paste electrode, drinking water safety

Introduction

Electrochemical DNA sensors apply single- or double-stranded nucleic acid chains immobilized on the surface of the working electrode which is the core of the analytical tool. This kind of sensor enhances significantly the sensitivity of the detection of chemical compounds revealing affinity to DNA strains. The accumulation of target molecules (analytes) in the receptor layer often results from the electrostatic attraction of positively charged cations to the negatively charged phosphate groups in the sugar-phosphate backbone of DNA. The application of nucleic acid strains in the sensor receptor layer may be also useful in the assessment of the genotoxicity of tested molecules, which bases on the evaluation of the changes in the electrochemical response of guanine and adenine, the purine bases present in DNA.

The pollution with toxic compounds that are able to change the structure and electric signal of nucleic acid is detected in a simple way showing the contamination scale of the environmental sample and the influence of analytes on bioactive compounds [Afonso et al. 2016, Bosch-Orea, Farré & Barceló, 2017]. Very good sensitivity of the electrochemical sensor is provided by voltammetric measurements carried out with the use of carbon working electrodes (e.g. carbon paste electrode, CPE or glassy carbon electrode, GCE) combined with platinum auxiliary and silver/silver-chloride reference electrode [Ligaj et al. 2014]. The problem in the commercial application of such an electrochemical array is its usability outside the laboratory with a portable potentiostat. Screen-printing is a popular method for mass production of disposable electrochemical sensors that are usually difficult to recover after measurement in conventional electrochemical arrays but they could be applied with small portable potentiostat [Metters, Kadara & Banks, 2011]. Screen-printed electrodes (SPEs) combine into one electronic structure classical three or two electrode array consisting of reference, working, and/or auxiliary electrodes on a small solid base. SPE electrodes based on carbon might replace so-called reusable bulk carbon electrodes (e.g. glassy carbon electrodes, GCE), which regeneration could be problematic. Similar advantages are also offered by inexpensive and easy preparation and application in DNA biosensors carbon paste electrodes (CPEs) [Fanjul-Bolado et al. 2008].

Rapid detection of hazardous compounds recognized also as environmental pollutants is of great importance [Lopes, Junior & Gutz, 2010]. The high risk presents heavy metals categorized as the most dangerous class of anthropogenic environmental pollutants. They can contaminate the environment, including water, also after wastewater treatment. In general, the highest concentration among the heavy metals from sludge is assigned for Pb, Hg, Cu, Cr, Ni, and Zn as determined

Al-Musharafi et al. [Al-Musharafi, Mahmoud & Al-Bahry, 2013]. One of the commonly occurring metals in the environment is copper. Copper is used to making building materials, electrical wiring, pipes, coins, and cooking utensils. It is present in alloys (brass, bronze) and coatings as well. Copper compounds are used in herbicides and wood preservatives, and azo dyes. Copper is used for engraving, lithography, petroleum refining, and pyrotechnics [WHO, 2004]. Copper is found in the consumed food: meat, offal, crustaceans, nuts, fruits, vegetables, mushrooms, whole grains, and also in drinking water. For living organisms copper is recognized as an essential trace element. It is an important component of cuproproteins required in many metabolic processes mainly associated with scavenging of free radicals, energy production, and neurotransmission [Prohaska, 2008, Lutsenko et al. 2010, Festa & Thiele, 2011]. Nevertheless, an excessive intake of the copper (II) ions can be an endangerment that causes adverse afflictions in people, including liver or kidney damage, gastrointestinal disturbance, coronary and cardiac muscle disease, and nervous system malfunctions like Parkinson's, Wilson's, and Alzheimer's diseases [Barnham & Bush, 2008, Festa & Thiele, 2011, Singh et al. 2013, Xu et al. 2017]. Long-term intake of high doses of copper is particularly dangerous because it can accumulate in the brain tissue and damage the blood-brain barrier.

The level of copper in tap water may be particularly dangerous due to having copper installations in households, which are recommended mainly due to bacteriostatic activity. Results from a number of studies from Europe, Canada, and the USA indicate that copper levels in drinking water can range from $\leq$ 0.005 to > 30 mg/L [WHO 2004]. The World Health Organization (WHO), U.S. Environment Protection Agency (EPA), and the Chinese Ministry of Health (CMH) regulate maximum permissible levels of copper (II) of less than 31 μM (about 1.9 mg/L), 20 μM (about 1.2 mg/L) and 15 μM (about 0.9 mg/L) in water [EPA. 2010, Xu et al. 2017], respectively. The European Union's standards give a limit of 2 mg copper in 1 litre of water intended for human consumption [Council Directive 98/83/EC 1998].

Considering the ubiquity of copper and its toxic impact on the human organism, it would be advisable to routinely control its content in drinking water, which is consumed daily by people. The determination of copper content in water samples can be performed using several instrumental methods and analytical techniques, such as atomic absorption spectrometry (AAS), inductively coupled plasma mass spectrometry (ICP-MS), inductively coupled plasma atomic emission spectrometry (ICP-OES), fluorescence spectrometry, adsorptive stripping voltammetry [Atanassova et al. 1998, Pourreza & Hoveizavi, 2005, Zhu et al. 2009, Lopes, Junior & Gutz, 2010, Feier et al. 2013, Soodan et al. 2014, Gumpu et al. 2015]. However, the majority of commonly used instrumental techniques are rather complicated, requiring sophisticated apparatus and highly qualified personnel. Their main limitation is the inability to use as handheld devices that are easy to use. The fast assessment of overall toxicity of heavy metals in water could be performed by biosensors that contain bioactive compounds or biological material in their receptor layer [Kanellis, 2018]. Some of them have been already commercialized, such as based on the utilization of *Vibrio fischeri* bacteria (Microtox®) or DNA-based HazardScreen® (HS®). However, they are not widely used devices, mainly because of their relatively high costs of the application and limited specificity towards particular metals. On the other hand, among the sensors designed strictly for the detection of copper contamination, various solutions can be found in the literature that offer detection limits ranging from ca. 0.6 nM to 15μM [Li et al. 2013, Kanellis, 2018]. Detection systems used in these sensors are based mainly on fluorescence techniques, voltammetry, inductively coupled plasma techniques, spectro-photometry, and colorimetric measurements [Chen et al. 2016, Kanellis, 2018]. Copper detection can also be carried out using electrochemical DNA sensors containing double-stranded nucleic acid fragments in their receptor layer [Bosch-Orea, Farré & Barceló, 2017]. The affinity of positively charged metal ions to the negatively charged backbone of DNA causes the accumulation of target molecules in the sensor's receptor layer, which increases the sensitivity of the conducted analyses. The electrochemical response of copper is associated with characteristic electric potential, which depends on the measurement conditions used, and enables its selective quantification. Particularly useful in qualitative studies of drinking water are portable devices enabling fieldwork on real samples. This possibility would be provided by electrochemical sensors based on disposable screen-printed electrodes [Lucarelli et al. 2002].

The work presents the comparison of three different screen-printed carbon electrodes (SPCEs) as usable detection elements for portable electrochemical sensor construction. The SPCEs applicability was compared with a self-made carbon paste electrode (CPE). All electrodes were tested in terms of the working range of electrochemical potential, reversibility of redox reaction, evaluation of the real (electrochemical) surface area and its roughness, the capacitance of the double-layer between the electrode surface and electrolyte. The sensitivity of the SPCEs was tested by the analysis of the oxidation signals of guanine obtained in the voltammetric measurement of oligonucleotides. The most promising SPCE was applied for the construction of a DNA biosensor designed for the detection of copper ions in real drinking water samples.

1. Material and methods

1.1. Apparatus, materials and chemicals

Electrochemical measurements were performed with potentiostat PGSTAT12 using GPES software, ver. 4.9 (Eco Chemie B.V., The Netherlands). Screen-printed carbon electrodes (SPCEs) performed by different manufacturers (Fig. 1) and carbon paste electrode (CPE) prepared by mixing graphite powder with mineral oil (70:30 w/w) were used for the sensor construction. Screen-printed carbon electrodes were provided by BVT Technologies (Czech Republic) – SPCE1, Institute of Electronic Materials Technology (ITME, Poland) – SPCE2, University of Florence (Italy) – SPCE3. All SPCEs combined three elements i.e. working electrode, reference, and auxiliary one, where the electrochemical array was printed onto corundum ceramic base (SPCE1) or onto polyester film (SPCE2 and SPCE3), respectively. The working carbon electrode was deposited in the centre of all printed electrochemical arrays (Fig. 1) with a diameter of 1 mm (SPCE1 and SPCE3) or 3 mm (SPCE2), respectively. A silver electrode was used as reference one in all SPCEs, whereas the auxiliary electrode was made from platinum in SPCE1 or graphite in SPCE2 and SPCE3. The dimensions of particular SPCEs electrodes were close to each other and presented as follows (height × width × thickness) – SPCE1: 25.4 mm × 7.3 mm × 0.6 mm; SPCE2: 33.0 mm × 14.0 mm × 0.2 mm; SPCE3: 26.0 mm × 7.0 mm × 0.5 mm.

CPE construction is based on the carbon paste made from graphite powder and mineral oil (70:30, w/w) and packed into Teflon® tube of 1 mm internal diameter. The electrical connection was supplied with a copper wire. The surface of this working electrode was always renewed before use by polishing to a smoothed finish on a weighing paper [Ligaj et al. 2014]. The CPE working electrode was used together with Ag/AgCl (3M KCl) reference electrode and platinum wire counter electrode in the three-electrode system for electrochemical measurement. The printed electrodes were single-use.

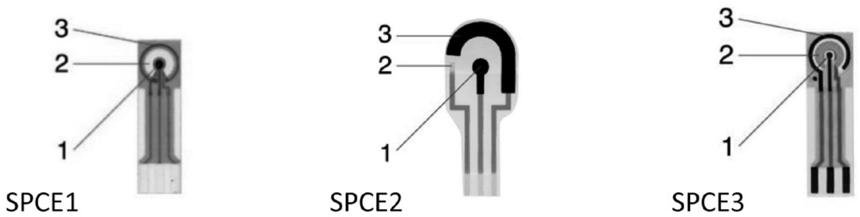

Fig. 1. Tested screen printed carbon electrodes (SPCEs). Explanation of SPCEs' elements: 1 – working electrode, 2 – reference electrode, 3 – counter electrode

Source: own study

All electrochemical measurements were performed in 50 mM phosphate buffer solution with the addition of 10 mM KCl (pH 7.00), which was also used as a washing buffer. Copper standard solutions of the appropriate concentrations (1, 2, 4, 6 and 8 mg / L) were prepared by diluting a certified copper standard (Merck Cat. No. 1197860100) at a concentration of 1 g / L with a 0.5 M HNO_3 solution. A solution of 0.5 M HNO_3 was used as a blank.

Measurements of atomic absorption spectrometry (AAS) were performed using the Varian AA800 (Varian, USA).

Chemicals: graphite powder, mineral oil, hexaammineruthenium (III) chloride (RuHex) were purchased from Sigma-Aldrich. The AAS standard stock solution of

Cu(II) was purchased from Merck. All other chemicals were from Polskie Odczynniki Chemiczne (Poland). Oligonucleotides at the sequence: 5'GTCAACTTC-CGTACCGAGC and 5'GCTCGGTA CGGAAGTTGAC were from Tib Molbiol (Poland). dsDNA was obtained after incubation of given above oligonucleotides at 40°C for 30 minutes in stirred phosphate buffer solution.

1.2. Methods

The cyclic voltammetry (CV) and square wave voltammetry (SWV) was used for electrochemical measurements. Experimental conditions were given in the description of the figures. For the presentation of all voltammograms Origin, version 8.0 (Microcal Software) was used. Calculations were executed on the ground average from three measurements.

Direct electrochemical measurements of copper on SPCE were done by immersing the electrode in the solution with a copper concentration from 1 to 8 mg/L for 90 seconds. The signal of oligonucleotides and dsDNA were measured after immersing the SPCE in a 10 μM sample solution for 600 seconds with the potential of +0.2 V applied for 30 seconds electrode followed by washing in the buffer. DNA sensor was obtained after dsDNA immobilization on the electrode surface and its immersion in a copper solution for 90 seconds. The signal of oligonucleotides and dsDNA on CPE were measured after the immersing of the three-electrode system in a 10 μM sample solution for 120 seconds with the potential of +0.5 V followed by 30-second electrode washing in the buffer. DNA sensor based on the CPE was obtained after dsDNA immobilization on the CPE surface, its immersion in a copper solution for the 90 s and 30 s washing in the buffer.

The construction of the portable DNA sensor is based on the receptor layer which is prepared by electrochemically supported adsorption of dsDNA molecules on the working electrode surface (with the potential of +0.2 V for 600 seconds) followed by the transfer of the electrode from the solution of dsDNA and leaving it to dry at ambient temperature. The sensitivity of performed DNA sensor was examined with drinking water samples fortified with copper (II) ions (AAS standard solution, Merck) in the concentration ranging from 0.1 to 8.0 mg/L. The concentrations of copper (II) ions in the solution were determined also by atomic absorption spectrometry. All measurements were made in triplicate at the wavelength of 324.8 nm in an air–acetylene flame. The sensor was examined with the use of three test water samples with an unknown concentration of the copper ions. The samples were enriched with sodium chloride in physiological concentration to check whether the increased ion content will not interfere with the electrochemical sensor, which was also tested by other researchers [Li et al., 2013].

2. Results and discussion

The electrodes were tested in the terms of the working range of electrochemical potential. All electrodes provided a clear and wide working potential (Fig. 2). The SPCE2 and SPCE3 electrodes revealed significantly lower values of capacitive current than SPCE1 and CPE ones which could be attributed to their less developed real surface which was examined in subsequent experiments (see table 2).

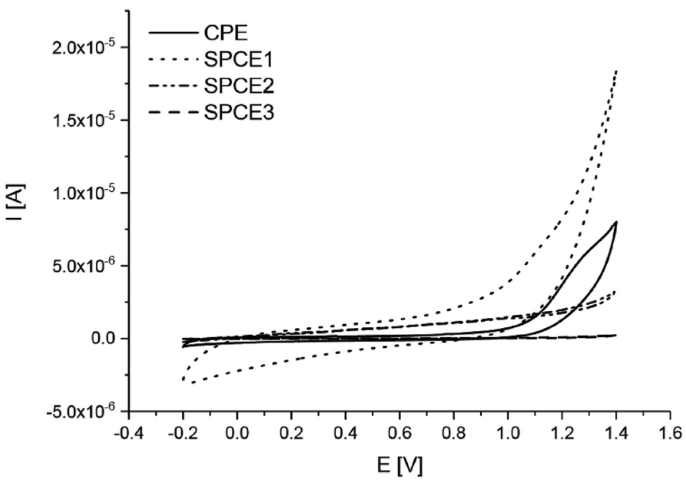

Fig. 2. CV voltammograms of all tested electrodes measured in 50 mM phosphate buffer with 10 mM KCl addition (pH 7.0), scan rate: 50 mV/s

Source: own study

Cyclic voltammetry (CV) measurements of 3 mM RuHex (hexaammine-ruthenium (III) complex) indicator in 50 mM phosphate buffer solution characterized the reversibility of redox reaction on all tested electrodes. Anodic current (Ia) and its potential (Ea), cathodic current (Ic) and its potential (Ec), potential difference, and current proportion from this experiment were presented in table 1. The highest indicator signal was provided by SPCE2 printed electrode but the least distorted electrochemical response (with the lowest ΔE) is observed for the CPE and SPCE1 electrodes.

Table 1. RuHex response in CV measurements performed on CPE and SPC electrodes

Electrode	I_a [μA]	E_a [V]	I_c [μA]	E_c [V]	ΔE [V]	I_c / I_a
CPE	4.46 ±0.02	1.153 ±0.002	4.59 ±0.08	1.092 ± 0.002	0.061 ± 0.004	1.03 ±0.02
SPCE1	3.16 ±0.08	0.979 ±0.004	3.40 ±0.15	0.919 ±0.005	0.060 ± 0.007	1.08 ±0.07
SPCE2	10.30 ±0.11	0.945 ±0.002	11.10 ±0.06	0.858 ± 0.002	0.087 ± 0.004	1.08 ±0.02
SPCE3	0.93 ±0.01	1.005 ±0.003	0.98 ±0.01	0.927 ± 0.002	0.078 ± 0.005	1.05 ±0.02

Source: own study

The electrochemical surface area and roughness factor of all tested working electrodes were determined using chronocoulometric measurements of RuHex (table 2).

Table 2. The results of electrodes' surface evaluation and capacitance of double layer between their surface and electrolyte

Electrode	Electrochemical electrode surface area (A) [mm²]	Geometric electrode surface area (G) [mm²]	Roughness factor (R = A/G)	Double layer capacitance (C) [μF/mm²]
CPE	1.32±0.03	0.79	1.68±0.04	25.2±0.1
SPCE1	1.36±0.04	0.79	1.73±0.05	212.2±2.3
SPCE2	8.92±0.27	7.01	1.26±0.03	0.2±0.1
SPCE3	0.930.02±	0.79	1.18±0.02	0.4±0.05

Source: own study

The most developed surface had SPCE1 printed electrode and CPE electrode. It is a very desirable characteristics, especially in relation to the application of the sensor for environmental analyses of trace contaminations. The double-layer capacitance was measured by the CV voltammetry technique for the electrodes immersed in 50 mM phosphate buffer solution. The highest tendency to generate background currents had SPCE1 screen-printed electrode with the highest capacitance value.

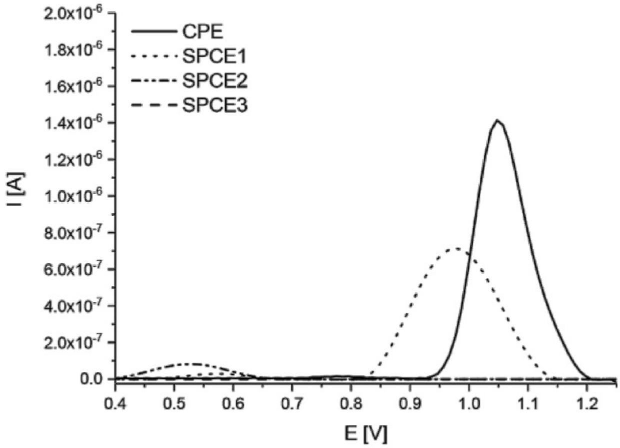

Fig. 3. SWV voltammograms (after baseline correction) of 10 μM oligonucleotide in 50 mM phosphate buffer with 10 mM KCl addition measured on tested electrodes. SWV parameters: frequency of 50 Hz, amplitude of 0.04 V and step potential of 0.01 V

Source: own study

All screen-printed electrodes were used in experiments that determined their usefulness as key element for the construction of the DNA sensor. The sensitivity of the electrodes was tested by performing square-wave (SWV) voltammetric measurements of the oligonucleotide with the sequence: 5' GTCAACTTCC GTACCGAGC. The resulting signals were compared to that obtained with the use of CPE (Fig. 3). Only SPCE1 screen-printed electrode gave well visible oxidation signal of guanine (at the potential of ca. +1 V). Their electrochemical response has a lower current and different position on the potential axis in comparison to the signal obtained using the

CPE electrode. However, the area of the resulting guanine peaks was similar in the quantitative analysis of the nucleobase obtained using both electrodes – SPCE1 and CPE.

The SPCE1 electrode was further applied to determine the copper (II) ions signal at the potential of ca. +0.1 V. The relationships between the SWV voltammetric current value and the concentration of the copper in the analyzed water solution was established (Fig. 4).

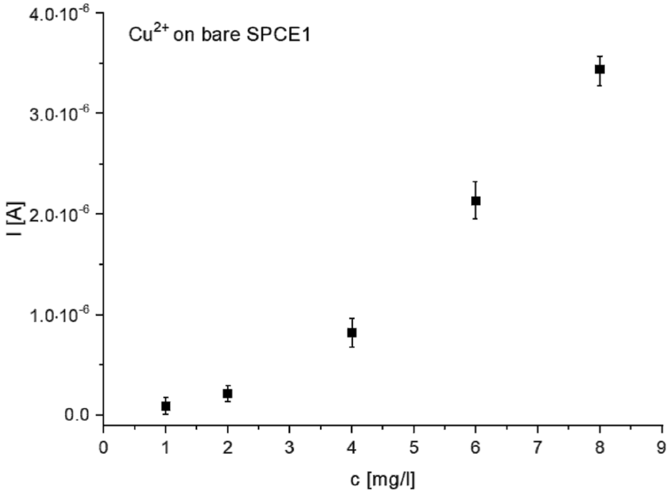

Fig. 4. Correlation between the copper concentration and SWV signal current obtained on SPCE1 in 50 mM phosphate buffer with 10 mM KCl and 14 mM CH3COOH addition. SWV parameters: frequency of 50 Hz, amplitude of 0.025 V and step potential of 0.005 V

Source: own study

Results presented in figure 4 showed that the tested SPCE can be used to construct a reliable sensor for the direct detection of copper (II) ions in concentration as low as 1 mg/L. However, for such low copper (II) concentration the SWV current was very low (in the range of 0.1 μA) and the results characterize significantly high relative standard deviation (RSD equalled 27% for five repeated measurements). Increasing the limits of quantitative detection to 2 mg/L the repeatability of analytical results increased substantially (RSD equalled 11% with the average current value of 0.3 μA for the copper concentration of 2 mg/L).

The SWV signals obtained for the copper concentration below 2 mg/L characterized a still relatively low current, therefore the next step of the sensor response was enhanced by the immobilization of dsDNA on the working electrode surface. The DNA-modified working electrodes were used for copper detection in drinking water samples to check the change in their sensitivity. The improved DNA biosensor has been able to detect the copper in a concentration below 1 mg/L (Fig. 5A) with a satisfactory value of the RSD precision index of 9%. Additionally, a significant increase in the guanine peak current was obtained after copper interaction with dsDNA immobilized in the sensor receptor layer which indicates the facilitation of its oxidation. This is probably the result of breaking hydrogen bonds stabilizing the double-stranded structure of dsDNA caused by copper ions [Theophanides & Anastassopoulou 2017]. A similar phenomenon was observed for the SWV measurements performed with the use of CPE (Fig. 5B).

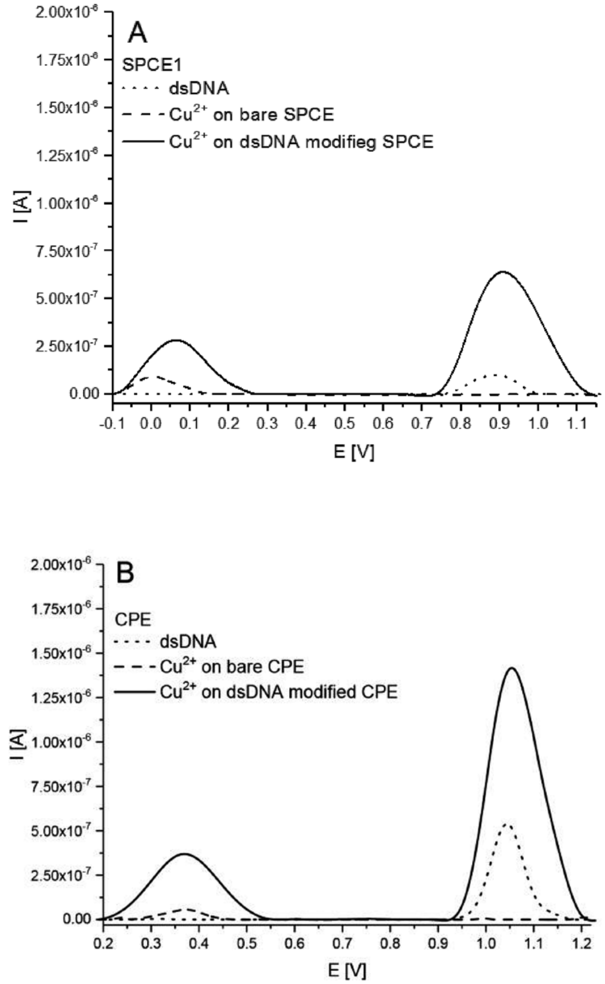

Fig. 5. SWV voltammograms (after baseline correction) of 10 μM dsDNA, Cu^{2+} [1 mg/l] on bare electrode and Cu^{2+} on dsDNA modified electrode in 50 mM phosphate buffer with 10 mM KCl and 14 mM CH_3COOH addition. The working electrodes used for sensor construction: A - the screen printed carbon electrode (SPCE1) and B - carbon paste electrode (CPE). SWV parameters as Fig. 4

Source: own study

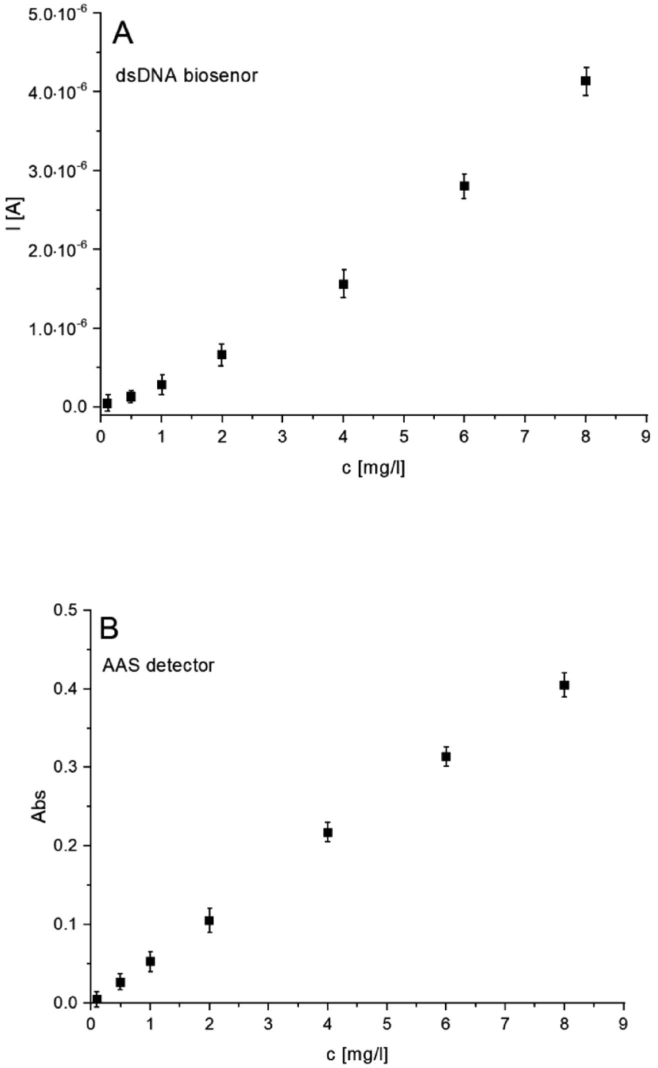

Fig. 6. Correlation between the copper concentration and: A - the SWV signal current obtained on SPCE1 in 50 mM phosphate buffer with 10 mM KCl and 14 mM CH_3COOH addition and B - the AAS signal

Source: own study

The final test was performed with the application of screen-printed electrodes with the working surface modified with electrodeposited dsDNA strands in the potential of +0.2 V. DNA-modified electrodes were left to dry at ambient temperature and stored in refrigerated conditions. Such prepared DNA sensors are ready to direct analysis of real water samples. The relationship between the height of the SWV signals obtained and the concentration of copper in the tested samples was determined. Measurements were made for drinking water samples containing from 0.1 to 8.0 mg/L of copper (Fig. 6A). Additionally, figure 6B summarizes the results of AAS measurements for the analysed water samples with copper addition.

Finally, the DNA biosensor with the SPCE1 electrode was tested in the measurements of the copper content in drinking water samples contaminated with the copper solution with an unknown concentration prepared in physiological saline. It also allowed checking whether the increased ionic strength will disturb electrochemical measurements performed using the sensor. The results of the analysis were compared with the results of AAS measurement of the same contaminated drinking water samples. The results of quantitative analysis by DNA sensor and AAS spectrometry were very similar to each other.

3. Conclusions

The detection of heavy metals is very important in monitoring environmental pollution. Presented electrochemical sensors enable fast and sensitive detection of metal ions in aqueous solutions. The high sensitivity of analyses was achieved using a self-made carbon paste electrode (CPE) which application enabled the detection of a trace of copper below 1 mg/L. Despite the high sensitivity, CPE can't be used in portable devices due to the susceptibility of its receptor layer to damage. Therefore, usable sensor construction with screen-printed carbon electrodes (SPCE) was tested. The working range of electrochemical potential, reversibility of redox reaction, evaluation of the real surface area and its roughness, the capacitance of double-layer, and electrode sensitivity were established. All parameters allowed to select the electrode most applicable for sensor construction. The electrochemical sensor provided with dsDNA fragments in its detection layer enabled copper (II) detection at a very low concentration of about 0.1 mg/L, but due to the high variability of the relatively low voltammetric signals received its practical quantification limit of copper (II) detection was established on 0.5 mg/L. The developed sensor was tested using drinking water samples containing an unknown copper content and an addition of 0.9% NaCl. It was shown that the sensor displayed tolerance to increased ionic strength. The results of voltammetric analyses provided by the DNA sensor were similar to those obtained with the AAS analyses of drinking water samples. The DNA sensor with the screen-printed electrode can be a portable device for checking the safety of drinking water monitoring in terms of copper ion content. It could be especially useful for water distributed in copper installations.

Fast and reliable tools for testing the quality of everyday products, especially water and food, are essential to ensure product quality and safety. It is especially visible in the face of ecological disasters or undesirable product adulteration. The development of easy-to-use and cheap analytical tools, such as electrochemical biosensors, enables ongoing control and effective supervision over product quality and safety. It also allows you to maintain good practices in the industry or supply chain, and take care of sustainable products that do not generate a negative impact on the environment.

4. Acknowledgements

All authors contributed to the study's conception and design. Electrochemical measurements were performed by Marta Ligaj and Mariusz Tichoniuk. The atomic absorption spectrometry were performed by Ryszard Cierpiszewski. The first draft of the manuscript was written by Mariusz Tichoniuk and Marta Ligaj. All authors developed and approved the final manuscript.

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