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EVALUATION OF NUISANCE OF ODOUR FROM FOOD INDUSTRY

An analysis of odour nuisance has been presented for a plant of food industry continuously and cyclically emitting pleasant odours. Odour emission was calculated based on odour concentration and volumetric flow rates of emitted gases. An indicatory model for odour propagation in air was used to evaluate the range of odour impact. The findings from questionnaire examinations made among inhabitants of housing estate in close vicinity of the plant were provided. Attention was paid to the need of classifying emissions from various sources based on hedonic quality of odours to determine the efficiency of odour emission removal.

1. INTRODUCTION

Odours are essential air pollutants, although in air protection they have been passed over for a long time. Even though posing no direct threat to human live, they may cause numerous health sufferings like headache, nausea, vomiting, or they may affect considerably general feeling of people subject to prolonged exposure of these contaminants. As there are no respective legal regulations for odour concentration levels, no odour reduction could be enforced on such plants. However, it is not easy to determine the admissible concentration levels for odours due to their specific properties. Apart from concentration and intensity of odours, which are in some way correlated, their important feature is the hedonic quality which distinguishes between “pleasant”, “neutral” and “unpleasant” categories. Beside the features of the odour itself, odour nuisance is an individual feeling of each human depending on a series of factors, including but not limited to age, health state, place of residence, sensitivity of the sense of smell, place and conditions of employment and other health-related, social

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and psychological aspects. Obviously, the time of exposure is also an important factor deciding on the odour nuisance.

In popular opinion, odour nuisance is associated with emission of unpleasant odours. As opposed to such circumstances, a plant was selected from food/biscuit industry due to its specific odours generated. Three operating process lines have been installed in the plant. Continuous baking is run in two daytime shifts. Hence, odour emission to atmosphere varies cyclically. The emission lasts about 12 hours and its intensity is virtually invariable. It should be emphasized that the odours emitted are considered to be pleasant. On account of this, the question arises if the odours generated from such a process could cause a significant nuisance and if such plants should be treated on a par with those generating unpleasant odours.

As a part of examining the plant's influence on olfactory quality of air, odour emissions were determined on the grounds of known odour concentrations and streams of gases. Odour concentrations were determined by the dynamic olfactometry method. Two methods were used to evaluate the influence of the plant on the surroundings: (i) by means of calculations using indicatory model and (ii) by questionnaire examinations among inhabitants of nearby housing estate. This allowed one to assess the range of pollutants generated by the plant and whether its activity causes considerable odour nuisance for local population.

2. PROFILE OF THE PLANT INCLUDING MAIN ODOUR SOURCES

The plant is situated in a ca. 50 thousand inhabitant town close to a large residential estate. The main products of the plant are biscuits and wafers. The plant is operated each day from Monday to Friday. There is no constant baking time schedule. The range of baked products is mainly dependent on the orders from customers. Only wafers are constantly baked each day. Baking of biscuits is a high-temperature process in the range of 150–220 °C and the main components are: wheat flour, sugar, eggs, vegetable fat, raising agents and essences which are to give proper flavour and smell to finished products [1, 2].

Based on the analysis of the baking process, two main reasons of odour emission can be distinguished:

- high temperature of processes used for components included in products,
- addition of food essences.

3. OLFACTOMETRIC EXAMINATIONS AND CALCULATION OF ODOUR

Olfactometric determinations were made to assess the emission of the plant. After visiting the the plant, following arrangements made with its representative, six sam-

pling points were selected (covered roof emitters). Their locations are shown in Fig. 1 while the specifications are summarized in Table 1.

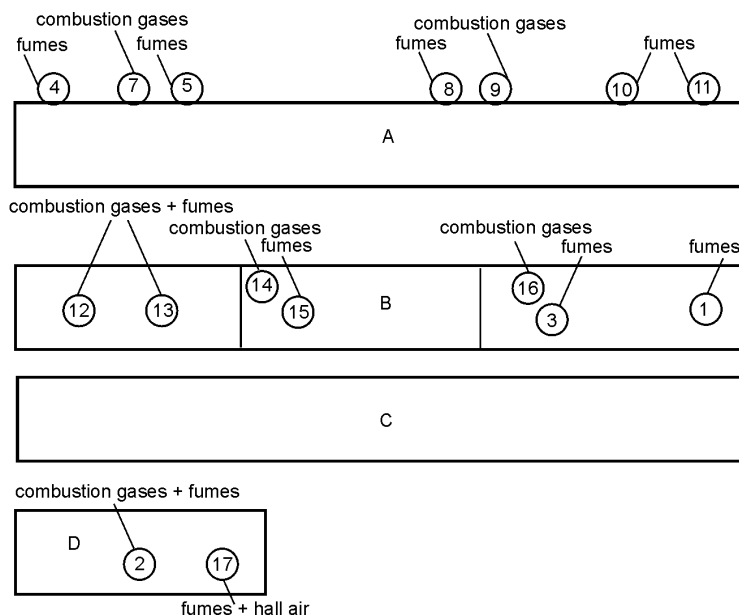


Fig. 1. Distribution of sampling points of odour gases:
 line A – Wyborowe biscuits with sugar, line B – Petit Beurre biscuits,
 line C – inactive line, line D – waffles

Table 1

Characteristics of the emitters

Emitter	Technological line	Product	Gas temperature [K]	Inner diameter ϕ [mm]	Gas stream at 293K [$\text{m}^3 \cdot \text{s}^{-1}$]
1	B	Petit Beurre biscuits	332	500	3.0
2	D	Waffles	398		3.4
3	B	Petit Beurre biscuits	423	250	2.2
4	A	Wyborowe biscuits with sugar	360		0.13
5	A	Wyborowe biscuits with sugar	384.5		0.13
6	hall ventilation	–	298	–	2,8

Four emitters under investigation were provided with ventilators (points 1 and 3 on the technological line B in Fig. 1, point 2 on line D and point 6 at the hall ventilation outlet). The two remaining emitters (points 4 and 5 on line A) operated on the principle of natural ventilation. Three gas samples were taken from each emitter. In total,

18 samples were collected in the plant. Olfactometric analyses of the samples were carried out on the day of sampling following the method given in the Standard PN-EN 13725 [3].

The measured values of odour concentrations, expressed in European odour units per cubic meter, ($\text{ou}_E \cdot \text{m}^{-3}$), are shown in Fig. 2. Determinations were made at the ambient temperature in the olfactometric laboratory (293 K).

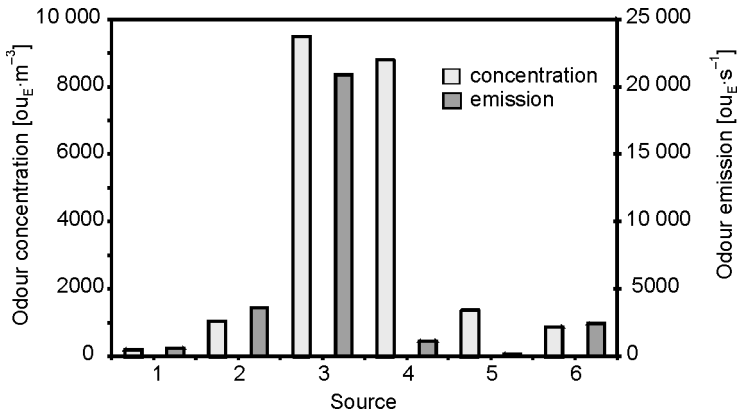


Fig. 2. Average odour concentrations and emission values

The rate of the odour emission, given in European odour units per second ($\text{ou}_E \cdot \text{s}^{-1}$) was determined based on the values of odour concentration and volumetric flow rates of emitted gases, in a similar way as for standard atmosphere pollutants. Measurements of volumetric flow rates using an anemometer were impossible due to lack of appropriate fixture branches to emitters, excessive temperature of gases and, in the case of emitters 4 and 5, due to natural ventilation applied. Hence, flow rates of gases discharged from emitters 1–3 and 6 were estimated using specifications of installed roof ventilators; in the case of emitters 4 and 5, volumetric streams were estimated from differences of temperatures (and densities) of waste gases and ambient air. Gas streams determined for all emitters were given at 293 K, i.e. at the temperature at which the odour concentrations were found. The results of calculations for odour emissions are shown in Fig. 2.

Figure 2 indicates that the highest odour concentrations were measured at points 3 and 4 (process lines B and A); quite large rates were also at point 2 on line D, i.e. on the wafer baking line, and in point 5 on line A. Calculations for emissions showed that the highest odour emission is observed for emitter 4, while emission of the emitter 5 is very low despite high concentration. It is due to natural ventilation applied; the gas stream is of one order of magnitude lower than that for mechanical ventilation. Significant emission was also noted from emitter 2 (wafer baking) caused by both high concentration of odours and high nominal capacity of the ventilator at the emitter.

4. EVALUATION OF ODOUR IMPACT RANGE AND ODOUR NUISANCE

The influence range of odours emitted from the plant was calculated based on the indicatory model of odour dispersion. Odour nuisance was estimated by means of questionnaire examinations. Calculations could also be made using the Pasquille formula, however no such accurate calculations are necessary to assess only the range of odour.

Results of calculation for indicatory model are given as odour concentrations (S_r [$\text{ou}_E \cdot \text{m}^{-3}$]) at a given distance x [m] from the source for various wind velocities u [$\text{m} \cdot \text{s}^{-1}$] [4]:

$$S_r = \frac{7E}{ux^2}$$

where E [$\text{ou}_E \cdot \text{s}^{-1}$] denotes odour emissions. The results of calculations are summarized in Table 2.

Table 2

S_r values [ou_E] obtained from calculations with using the indicator model

u [$\text{m} \cdot \text{s}^{-1}$]	x [m]				
	100	150	200	500	1000
0.5	40.4	17.9	10.1	1.6	0.40
1	20.2	9.0	5.0	0.8	0.20
2	10.1	4.5	2.5	0.4	0.10
3	6.7	3.0	1.7	0.3	0.07
4	5.0	2.2	1.3	0.2	0.05
5	4.0	1.8	1.0	0.2	0.04
6	3.4	1.5	0.8	0.1	0.03
7	2.9	1.3	0.7	0.1	0.03
8	2.5	1.1	0.6	0.1	0.03
9	2.2	1.0	0.6	0.1	0.02
10	2.0	0.9	0.5	0.1	0.02

Results of calculations given in Table 2 show that odours can affect surroundings within as much radius as even 500 m ($S_r > 1 \text{ ou}_E \cdot \text{m}^{-3}$) [5]. Hence, conclusion may be drawn that emission should be reduced. However, an important fact is that these odours are classified as pleasant ones. On account of that, can the plant be an essential source of odour nuisance? The answer to the question should be verified by the results of field inspections and/or surveys in accordance with the methods used in European countries and currently being developed in Poland [6–12].

In the presented work, questionnaire examinations of odour nuisance were used to determine the influence of odour emission from a plant on the odour quality of air in its surroundings. The area of examinations was delimited from calculations of the odour range, and also from spatial development and topography of the area around the plant. The method given in VDI 3883 [6] was used to conduct a survey on odour nuisance among people living near the plant. Data were collected in interviews with residents by trained personnel. Attempts were made to contact with 164 people, however no more than 58 questionnaires were obtained, i.e. ca. 35% (Table 3).

Table 3

Sample size of conducted surveys

Zone	Net sample size, n	Gross sample size, N	Survey missed	
			No tenant	Refuse to answer
1 + 2	58	164	75	31

The questionnaire contained ten questions referring to reaction to the environmental state, arduousness of pollution and socio-demographic aspects. Respondents were also asked about their personal data, such as age, education level and distance between place of work and place of residence [6].

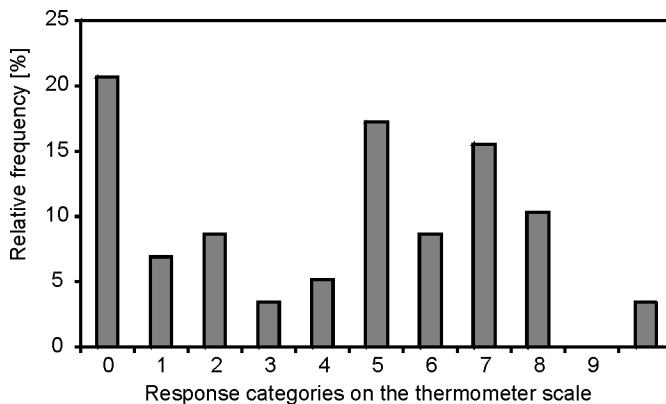


Fig. 3. Odour nuisance indicated by the respondents on the thermometer scale

In the questionnaire, the most important questions were those about evaluation of annoyance in thermometer and in verbal scales. Respondents were asked to identify the odour nuisance by the number on a scale of 1 to 10. The results are shown in Fig. 3.

Based on questionnaire examinations, a conclusion might be drawn that the plant represents an essential odour nuisance. However, in further question respondents are asked to point out the source or the nature of the odour. This question allows one to

determine whether the plant under examinations is in fact the source of nuisance, or there is another factor nearby which deteriorates the odour quality of air in the area (Fig. 4).

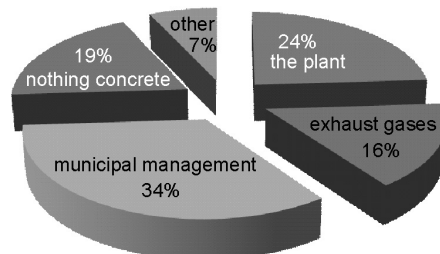


Fig. 4. Odour sources indicated by the respondents

As results from Figure 4, as a source of odour the plant is indicated by as low as 24% of people polled, whereas 50% indications referred to municipal management and exhaust gases. It should be also stressed that there is municipal sewage treatment plant located about 1.3 km to the east, and a national road leading to motorway is running 300 m from the plant.

Additionally, the questionnaires were split into: (i) those made in two residential buildings situated at the shortest distance from the plant, and what is worth mentioning – being high multifamily apartments, and (ii) those made in buildings located at larger distances within the area covered by questionnaire. Such division allowed one to determine wherefrom are the highest percentage of indications to the plant. The closest buildings shared 71% of all indications to the plant.

The questionnaire examinations have also shown that odours from the plant, however quite perceptible, are not bothersome for local people. The smells were generally described as sweet, vanilla, chocolate-like and were included into pleasant smells and, in quite large of cases, as those which do not deteriorate life quality among respondents.

5. SUMMARY

The main reasons for odour emission in cake-production industry are high baking temperature and flavours added to enhance taste and smell values of finished products. Odour emission from selected emitters, calculated from odour concentrations as measured by the dynamic olfactometry method and from estimations of gas volumetric streams, is quite large and can be significant in plant surroundings, as was confirmed by approximate calculations using an indicatory model.

The results from questionnaire examinations were divided into those obtained from successful questionnaires from respondents living in two high apartment blocks situated ca. 100 m to the north of the plant and those for the rest of polled area. Conse-

quently, a conclusion may be drawn that these blocks represented some kind of screens greatly hindering dispersion of odours into the housing estate. Only the occupants of these blocks were those who complained about arduousness of odours from the plant due to their intensity, often describing them as nauseous.

Based on the evaluation made for odour impact of source emitting odours perceived as pleasant ones, a proposal could be made to take into account, while preparing legal regulations on odour emission, the branch of industry to which belong the plant investigated, the kind of production and its parameters. This would permit to reduce serious odour nuisance effectively, while not exposing such plants, generating pleasant smells which cause no essential change in life quality of local people, to the risk of losses.

ACKNOWLEDGEMENTS

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JÓZEF KUROPKA*

REMOVAL OF NITROGEN OXIDES FROM FLUE GASES IN A PACKED COLUMN

The state of technology and the possibilities of removal of nitrogen oxides from flue gases in alkaline solutions with oxidants have been presented. The results of the research on the absorption of nitrogen oxides in alkaline solution of sodium hypochlorite in a packed column showed high efficiencies of removal of nitrogen oxides in a wide range of the following parameters: gas velocity, spraying density, concentration of nitrogen oxides in gas and concentration of spraying solution.

1. INTRODUCTION

Nitrogen oxides belong to the most troublesome gaseous components polluting atmospheric air. Among several nitrogen oxides (N_2O , NO , N_2O_3 , NO_2 , N_2O_4 , N_2O_5), the most common in atmospheric air are nitrogen oxide (NO) and nitrogen dioxide (NO_2). In chemical engineering and combustion techniques, their total content ($NO + NO_2$ converted to NO_2) is marked with a common symbol NO_x [1]. Those pollutions are heavily toxic for human environment taking parts in forming photochemical smog.

Nitrogen oxides accompany all combustion processes of solid, liquid and gas fuels, therefore power industry, heat engineering and transport are the main and most serious source of those pollutions (Table).

The sources of emissions of NO_x to atmospheric air are also industrial technologies which emit nitrogen oxides as a result of certain chemical reactions. This includes mostly chemical plants producing nitric acid and fertilizers, sulfuric acid by the nitric method, and nitric acid derivatives in organic syntheses. Moreover, the sources of emissions of nitrogen oxides are all reactions of surface pulping of metals in nitric acid. Those sources pose a major threat for natural environment because of their sometimes substantial local concentration.

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Table

Emission of nitrogen oxides in Poland as NO₂ [2]

Emission sources	1990	1995	2000	2007	
	[Gg·year ⁻¹]				[%]
Commercial power industry	370	377	237	249	28.1
Industrial power industry	130	111	81	101	11.7
Industrial technologies	200	103	109	73	8.2
Stationary sources ^a	100	115	97	113	12.7
Mobile sources	480	414	314	349	39.3
Total	1280	1120	838	885	100.0

^aLocal boiler houses, domestic hearths, craft workshops etc.

The majority of more important sources emit to atmospheric air gases of low degree of oxidation, which highly complicates removal of nitrogen oxides from exhaust gases and from industrial flue gases [1].

2. METHODS OF REMOVAL OF NITROGEN OXIDES FROM GASES. STATE OF TECHNOLOGY

Methods of removal of nitrogen oxides from flue gases applied in recent years belong to the following groups [1]:

- catalytic reduction (non-selective catalytic reduction (NSCR) and selective catalytic reduction (SCR)),
- adsorption,
- absorption (acid and alkaline).

Catalytic reduction is an efficient but very expensive method of gas treatment. It is used mainly in highly industrialized countries to neutralise nitrogen oxides from energetic exhaust fumes and from industrial flue gases, which are formed during production of nitric acid. This method requires using catalysts and, as reducing gases: hydrogen, carbon oxide, methane and other hydrocarbons, as well as ammonia reacting selectively with nitrogen oxides in the presence of oxygen. This method is currently not commonly applied in Poland, mainly due to substantial investment and exploitation costs. The cost of reactor results mainly from the demand for catalyst mass (depending on concentration of nitrogen oxides in gases), it depends on the catalyst vitality and on consumption of reducing gases and on the annual number of working hours at full load [1].

Despite high efficiency, adsorption methods exploiting traditional adsorbents have not been commonly used in installations for removing nitrogen oxides from industrial flue gases, mainly for economical reasons and because of difficulties connected with

regeneration of adsorbent or its utilization. Technology of cleaning flue gases from nitrogen oxides on anion exchangers [1] elaborated by the author is advised for neutralising nitrogen oxides from small emitters characterised by variable emission. Typical of this technology is a powerful tolerance for nitrogen oxides in the gas treated with maintaining high efficiency of treatment, as well as its simplicity and user-friendliness of the apparatus.

Methods of absorption of nitrogen oxides in solutions belong to the earliest ones in technology of industrial flue gases treatment. Those methods are based on fundamental properties of nitrogen oxides present in gases: their solubility in water [3, 4] or in solutions of nitric acid [5, 6] and sulfuric acid [7–9] as well as their ability to form appropriate salts, nitrates and nitrites in reactions with substrate of alkaline character [10–17].

Absorption of nitrogen oxides in acids leads to producing of nitric acid or concentrated nitrogen oxides, thus application of such methods does not lead to formation of side-products but only to increase of the amount of the basic product. In most cases, the methods are not complicated in terms of chemical and processes engineering. Their shared defect is too slow mass transfer, which demands big capacities of apparatuses in industrial conditions. Many other corrosion problems are linked to these methods, which is usually omitted in the works on laboratory scale.

On the other hand, methods of absorption of nitrogen oxides in alkaline solutions are generally rated higher in terms of efficiency. They are usually more expensive because the products require further technological proceedings. Absorption methods, however, provide decrease of content of nitrogen oxides in industrial flue gases to the extent defined by sanitary norms.

Generally, absorption methods are characterised by a simplified technological outlines and simple, typical apparatuses. Running of the process does not also cause substantial problems with their exploitation. Specialised sources, however, do not provide essential information on designing installations for purification of flue gas from nitrogen oxides.

3. ALKALINE ABSORPTION OF NITROGEN OXIDES

Application of the alkaline absorption to protect environment is determined by physicochemical properties of nitrogen oxides. Nitrogen dioxide has sufficiently high solubility and reactivity with water and with aqueous alkaline solutions, and as such it can be absorbed in solutions [1, 10–17]. Nitrogen oxide is poorly soluble in water and its reactivity with alkaline solutions is low. To remove nitrogen oxide from gases by the absorption method in solutions, it should be oxidized to nitrogen dioxide in accordance with the following reaction:



If the volume of NO in the mixture of NO and NO₂ will be equal to or smaller than the volume of NO₂, in consequence of contact with alkaline solution such as NaOH, the outcome will be total absorption of both oxides in accordance with the following reaction:

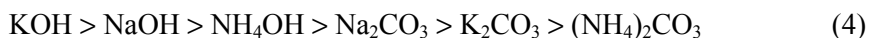


At the excess of nitrogen dioxide, apart from the processes described by Eq. (2), nitrogen dioxide will react with NaOH as follows:



At the excess of nitrogen oxide, only the number of molecules of nitrogen oxide equivalent to nitrogen dioxide will react (2), whereas the remaining NO will not react with NaOH and will remain in the gas phase.

Atroščenko [10] found that the mixture of nitrogen oxides of the volume ratio of NO₂ to NO higher than or equal to unity, is absorbed with the highest rate in alkaline solutions. It was confirmed by Głowiński et al. [17]. The role of concentration and type of absorption liquid on the absorption rate of nitrogen oxides was studied by Kuznecov [11]. He stated that the change of the initial concentration of the studied solutions from 10 into 100 g/dm³ increases the rate of absorption by 4–5 times. Kuropka established a sequence of activities of alkaline solutions used for the absorption of nitrogen oxides, which diminishes in the following order [1, 15]:



The influence of concentration of absorbing solution on the absorption of nitrogen oxides was different for the examined solutions. For the solution of NaOH, violent impact of the solution's concentration on the absorption efficiency reached the value of 2 wt. %, and for the solution of sodium carbonate it reached the value of 10 wt. %.

The mechanism of the absorption process of nitrogen oxides in alkaline solutions was examined also by Aoki [13] and Carta [14]. They determined the speed of nitrogen oxides absorption in NaOH solutions and the influence of nitrite ions on the process of absorption.

3.1. ALKALINE ABSORPTION OF NITROGEN OXIDES WITH OXIDANTS

Attempts were made to solve the problem of raising the level of oxidation of nitrogen oxides by absorption with simultaneous oxidizing of nitrogen oxides with compounds which easily release oxygen in the liquid phase. Useful for these purposes proved to be compounds with strongly oxidizing properties, such as sodium hypochlorite [1, 15], sodium chlorite [18–20], calcium hypochlorite [21], potassium permanga-

nate, and potassium dichromate [1, 15, 22], salts of iron, copper, nickel and cobalt [1, 15, 23, 24] and hydrogen peroxide [1, 15, 25].

The research on absorption of nitrogen oxides in alkaline solutions of sodium hypochlorite (NaOCl) have been presented elsewhere [1, 15]. It was determined that the level of absorption of nitrogen oxides is over 90%, and the process itself runs almost with the stoichiometric ratio in terms of the sorption capacity of the solution.

Mechanism and kinetics of the NO_x absorption in alkaline solutions of sodium chlorite was studied by Sada [18, 19]. He stated that the reaction rate decreases exponentially upon increasing NaOH concentration. Too low concentration of OH^- ions causes degradation of sodium chlorite to gaseous chlorine dioxide, which next in the gaseous phase oxidizes nitrogen oxide. Sada claims that to stop degradation of NaClO_2 and provide absorptive liquid with constant oxidizing property, concentration of OH^- ions must be maintained at a constant level. He suggests, then, to use sparingly soluble alkaline hydroxides: $\text{Ca}(\text{OH})_2$ or $\text{Mg}(\text{OH})_2$.

Furuta removed nitrogen oxides from flue gases using solutions of calcium hypochlorite of the concentrations of 3–15 g/dm^3 [21] with 95–100% efficiency. Using hydrogen peroxide in a packed column in a laboratory scale [25] lead to the conclusion that the efficiency of NO_x absorption is low (4.5–9%), allowing, however, to treat gases which contain 0.5–1.0 vol. % of nitrogen oxides with 85–95% efficiency.

Great interest was evoked by the possibility of removing NO_x from flue gases in alkaline solutions (NaOH , Na_2CO_3 , $\text{Ca}(\text{OH})_2$) with the use of ozone as an oxidants in gaseous phase. Dimov [26] states that high efficiency of absorption is possible to be obtained at relatively slight ozone consumption. Pronounced effect is reached by using ozone in the absorption of nitrogen oxides of low concentration. The appropriate apparatus for this process is a packed column. Because of very high rate of oxidation, ozone is added to gases immediately before the absorption column. The efficiency of absorption at the gas velocity of ca. 4 m/s exceeds 95% [26].

In the paper, substantial parameters have been determined of the process of removing nitrogen oxides from gases in a packed column sprayed with alkaline solution with the addition of sodium hypochlorite were presented.

4. CONDITIONS OF EXPERIMENTS AND RESULTS OF THE RESEARCH

In the experiments, a packed column 1.0 m high and 0.025 m in diameter was used. Details concerning the installation have been described elsewhere [1]. Variable parameters were as follows:

- gas volume stream $(4.9\text{--}49.0)\cdot 10^{-5} \text{ m}^3/\text{s}$,
- gas velocity 0.1–1.0 m/s,
- initial concentration of NO_x (converted to NO_2) in gas 1.0–10.0 g/m^3 ,

- volume stream of spraying solution $(6.8\text{--}54.4)\cdot 10^{-7}\text{ m}^3/\text{s}$,
- spraying density $5\text{--}40\text{ m}^3/(\text{m}^2\cdot\text{h})$.

Various types of packings were used as well as and various spraying solution differing also in concentrations. During a single experiment with a given type of a packing and a given type and concentration of the spraying solution, the gas volume stream was maintained at a constant level, whereas the initial NO_x concentration (converted to NO_2) in the gas and the volume stream of the spraying solution were changed. In the examined range of variable parameters, the averages from 3 measurements were taken into account.

The possibility of increasing the efficiency of NO_x absorption in 5 wt. % solutions of NaOH [1] was tested by adding NaOCl, H_2O_2 and KMnO_4 as oxidants to the spraying solution. The influence of basic process parameters such as gas velocity, concentration of nitrogen oxides in gas, concentration of oxidants in spraying solution and spraying density on the absorption efficiency has also been tested.

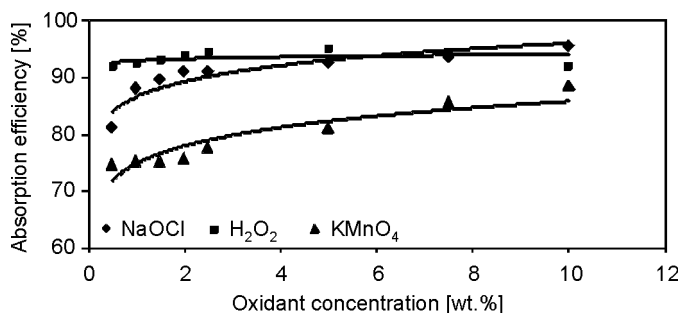


Fig. 1. Effect of the addition of oxidant into 5 wt. % solution of NaOH on the absorption of nitrogen oxides at constant initial concentration of NO_x of $3.5\text{ g}/\text{m}^3$ gas, gas velocity of $0.2\text{ m}/\text{s}$ and spraying density of $20\text{ m}^3/(\text{m}^2\cdot\text{h})$

In Figure 1, the effect of addition of an oxidant into NaOH solution on the efficiency of absorption of nitrogen oxides was shown. The concentration of the oxidant in 5 wt. % solution of NaOH was changed in the range from 0.5 to 10 wt. %. During an experiment for a given type of spraying solution, the gas velocity of $0.2\text{ m}/\text{s}$, spraying density of $20\text{ m}^3/(\text{m}^2\cdot\text{h})$ and initial NO_x concentration of $3.5\text{ g}/\text{m}^3$ in the gas cleaned were maintained. In the examined range, the efficiency of the absorption of nitrogen oxides was increasing upon the increase of the oxidant concentration. This is most evident for hydrogen peroxide, then for sodium hypochlorite and potassium permanganate. The effect of NaOCl concentration is mainly visible up to 2 wt. %, the dependence is linear above this value (similarly as for hydrogen peroxide and potassium permanganate), and further increase of NaOCl concentration causes slight increase of the process efficiency.

Exemplary dependence of the efficiency of absorption of nitrogen oxides on the gas velocity for NaOCl oxidizing solutions with various contents of the oxidant is shown in Fig. 2.

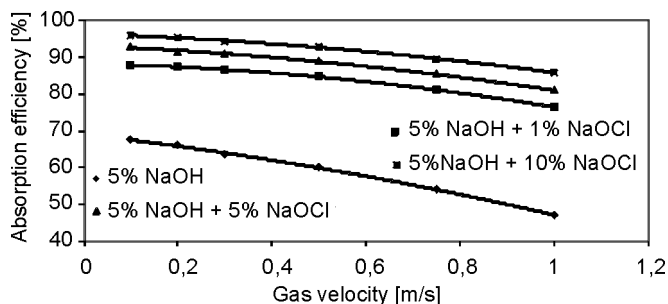


Fig. 2. Dependences of the absorption efficiency of nitrogen oxides on the gas velocity for solutions with various contents of NaOCl at constant initial concentration of NO_x of 3.5 g/m^3 of gas, gas velocity of 0.2 m/s and spraying density of $20 \text{ m}^3/(\text{m}^2 \cdot \text{h})$

The efficiency of the process decreases upon increasing the gas velocity; the shape of the curves is similar for all types of spraying solutions. The effect of addition of NaOCl to the basic NaOH solution is evident from Fig. 2. For example, using of 1 wt. % of NaOCl at the gas velocity of 0.2 m/s , increases the efficiency of the absorption by 21.4%, whereas at the gas velocity of 0.8 m/s , it increases by 27%. From the dependences shown in Fig. 3, it can be observed that increasing the spraying density improves the efficiency of absorption of nitrogen oxides in alkaline solution of NaOCl by 4–6%.

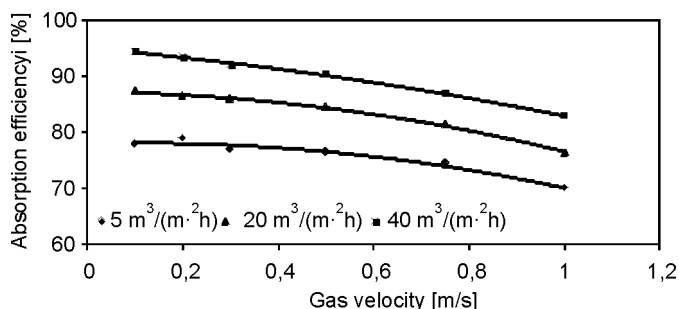


Fig. 3. Dependences of the absorption efficiency of nitrogen oxides on the gas velocity for various spraying densities with 5 wt. % solution of NaOH with the addition of 1 wt. % NaOCl at constant initial concentration of NO_x of 3.5 g/m^3 of gas)

Upon the increase of NO_x concentration in the gas treated, the efficiency of the process increases linearly, while the increase of the efficiency of treatment is not known (Fig. 4). Using various heights and kind of packings in a column confirmed [1] that the efficiency of the absorption increases upon the increase of the contact time of the gas with the absorption solution. Using spraying between the layers of the packing and applying packing of an increased specific surface area improves the efficiency of the process by a few percent [1, 8, 15]. Applying packings with an increased specific surface area limits resistances of the gas flow influencing the economics of the installation.

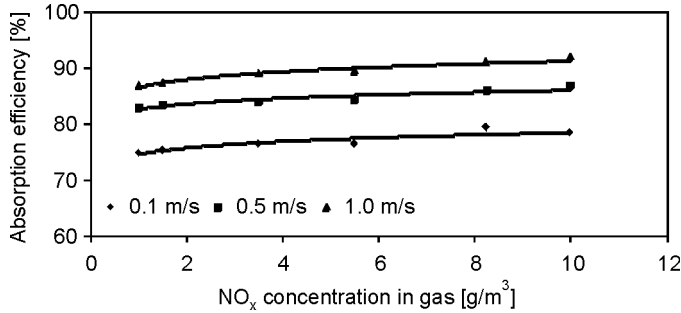


Fig. 4. Dependences of absorption efficiency of nitrogen oxides on their concentration in gas for various gas velocities, at the spraying density of $20 \text{ m}^3/(\text{m}^2 \cdot \text{h})$ with 5 wt. % solution of NaOH with the addition of 1 wt. % of NaOCl

Technological experiments under industrial conditions [1] confirm that the efficiency of the absorption of nitrogen oxides does not depend on NaOH concentration in the absorptive solution, whereas NaOCl concentration greatly influences the efficiency of the absorption. Consumption of absorptive solution to absorb 1 kg NO_x (converted to NO₂) was 1.645 kg of NaOCl and 0.891 kg of NaOH.

Quantitative description of the process of mass transfer with incorporating the so-called efficiency of absorption was used. The efficiency of absorption allows one to estimate in a very simple and clear way the influence of basic parameters of the process on the efficiency of gas treatment. It was assumed that the efficiency of the absorption is the function of the following variables:

$$\eta = f(w_{og}, L, c_{og}, c_r) \quad (5)$$

where: η – efficiency of absorption, %, w_{og} – gas velocity calculated for the diameter of the empty column, m/s, L – density of spraying, $\text{m}^3/(\text{m}^2 \cdot \text{h})$, c_{og} – initial concentration of NO_x (converted to NO₂) in gas, g/m^3 , c_r – concentration of the absorptive solution, kg/m^3 or wt. %.

For the examined range of variable parameters, the determined values of the efficiency of absorption η were plotted as the following functions:

$$\eta = f(w_{og}), \quad \eta = f(L), \quad \eta = f(c_{og}), \quad \eta = f(c_r) \quad (6)$$

After analysing the plots, the effectiveness of mass transfer was shown as the following function:

$$\eta = 1 - \exp(-f(\text{process variables})) \quad (7)$$

In the examined case, the following dependence was obtained:

$$\eta = 1 - \exp(-f(w_{og}, L, c_{og}, c_r)) \quad (8)$$

and it was used as the function:

$$\eta = 1 - \exp \left(-B_0 (w_{og})^{B_1} (L)^{B_2} (c_{og})^{B_3} (c_r)^{B_4} \right) \quad (9)$$

The coefficients B_i were assigned by the linear multiple regression method. In the examined range of the variable parameters for the absorption of nitrogen oxides in alkaline solutions of NaOCl, the following relation was defined:

$$\eta = 1 - \exp \left(-0.682 (w_{og})^{-0.152} (L)^{0.229} (c_{og})^{0.068} (c_r)^{0.033} \right) \quad (10)$$

for which the multiple correlation coefficient R equals 0.88, and the mean error is 4.91%.

5. SUMMARY

Research on the absorption of nitrogen oxides in alkaline solutions with oxidants allowed one to examine the influence of basic process parameters such as: gas velocity, concentration of nitrogen oxides in gas, concentration and type of solution and spraying density, on the process of gas treatment.

Experimental data verifies reports from specialised literature and provides essential knowledge on designing installations for removing nitrogen oxides from gases.

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METHOD OF SIMULTANEOUS MEASUREMENT OF TOTAL SULFUR, CHLORINE AND FLUORINE CONTENT IN BIOGAS

The method of determination of total content of sulfur, chlorine and fluorine compounds in biogas has been implemented and verified at real conditions. The laboratory plant and the results of periodical measurements of the composition of biogas have been described. The main effects of the research are: determination of the range of concentrations for the analysed compounds in a typical biogas from sewage sludge digestion and evaluation of average fraction of sulfur from hydrogen sulfide in total sulfur content during multiannual period.

1. INTRODUCTION

New analytic methods for evaluating biogas composition and its properties need to be implemented to respond to intense development of biogas plants expected in the nearest future in Poland [1]. Energy producing combustion, being the basic method of biogas utilization, requires its conditioning so as to eliminate any risk for combustion equipment and environmental hazard as well. This means that apart from evaluating basic process parameters such as: chemical constitution (the content of CH₄, CO₂, N₂, O₂, H₂, H₂O), calorific value, gross calorific value, Wobbe index which can be determined with a sufficient accuracy on the grounds of standards for natural gas, it would be necessary to use specific methods for numerous compounds of sulfur, chlorine and fluorine being present in the biogas. So far, no such methods for biogas were developed. Well known methods applicable to determining the content of sulfur compounds based on combustion [2, 3] which could be adapted to this purpose, have numerous inconveniences. In Wickbolds' method, a sample is burnt out in hydrogen/oxygen flame, hence its inherent drawbacks include risk of explosion (especially during process initiation) and high costs of used gases. The method provides no way of tempera-

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ture regulation and control within combustion zone which could lead to incomplete combustion. Variable composition of biogas and related fluctuations of calorific value create additional problems with maintaining proper hydrogen/oxygen/gas proportions and stability of combustion processes. In Lingener's method, combustion takes place in air without any additional fuel. Also in this case, no control and regulation of combustion temperature exist. While an analysis is made using this standard, we shall expect lower combustion temperatures than those for natural gas, which can lead to incomplete oxidation of sulfur.

Bearing this in mind, an idea was arisen in the Environmental Protection Institute of Wroclaw University of Technology to develop a method free of the above disadvantages allowing simultaneous measurement of total content of sulfur, chlorine and fluorine in biogas. The method based on flameless combustion of biogas in air followed by spectrophotometric and/or chromatographic analysis of combustion products was proposed. To this purpose, a testing system was built up and also the parameters of combustion processes and sampling procedure were experimentally developed. The system was then used to determine the composition of biogas taken from municipal sewage treatment plant with throughput of ca. 80 000 m³/day [4].

2. HAZARDS PROMPTED BY BIOGAS AND ITS BURNING PRODUCTS

Typical composition of dry biogas generated from sludge digestion is as follows: CH₄ (ca. 65%), CO₂ (ca. 34%), and the rest (ca. 1%), including: N₂, O₂, H₂, H₂S, NH₃, hydrocarbons (C₂–C₇) and trace substances such as compounds of sulfur, chlorine and fluorine. Sulfur can be present in biogas as inorganic compounds (mainly hydrogen sulfide) and also organic compounds (mercaptans, thioethers, thiophene and derivatives, carbon oxysulfide, dimethyl sulfides, and others). A basic source of H₂S is biochemical, anaerobic digestion of sulfur compounds originating from animal organisms, mainly proteins, while sulfur organic compounds are primarily of plant origin. Halogens are generally coming from impurities in sewage. Chlorine compounds may also originate from chemicals used for water purification and sewage treatment. Exemplary compounds of chlorine and fluorine found in biogas are as follows: chloroethane, dichlorofluoromethane, trichlorofluoromethane, chlorotrifluoromethane, trichloromethane, tetrachloroethane, trichloroethane, dichloromethane, dichloroethane, dichloroethene, dichloropropane, carbon tetrachloride, chlorobenzene, dichlorobenzene, tetrachloroethylene, vinyl chloride, etc. [5].

Compounds of S, Cl and F are the most difficult for treatment and cause the highest environmental nuisance among substances found in biogas. Combustion products from these compounds are aggressive for equipment and environment. Also H₂S is distinguished by its corrosive properties. It can also increase fire and explosion hazard as it reacts with iron, leading to generation of self-igniting ferrous sulfide. When bio-

gas containing sulfur compounds and halogens is subject to combustion in gas engines, it causes engine oils life to be shortened and catalyst activity to be reduced.

Table

Admissible concentrations of sulfur and halogen compounds in biogas

Substance	Admissible limit	Country	Reference
Hydrogen sulfide	5 mg/m ³	–	[6]
	200 mg/m ^{3b}	–	[9]
	0.15 vol. %	–	[10]
	5 mg/m ³ 20 mg/m ³ 20 mg/m ³	Germany Hungary Poland	[7]
	6 mg S/m ³	Denmark, Sweden	[8]
Total sulfur	50 mg/m ³	–	[6]
	2000 (1150 ^a) mg H ₂ S/10 kWh	–	[9]
	2200 mg/m ³ CH ₄	–	[10]
	120 mg/m ³ 100 mg/m ³ 40 mg/m ³	Germany Hungary Poland	[7]
	120 mg/m ³	Denmark, Sweden	[8]
Total halogens	5	–	[6]
Total Cl +2×total F	100 (0 ^a) mg/10kWh 100 mg/m ^{3b}	–	[9]
	Cl F Cl + F	100 mg/m ³ CH ₄ 50 mg/m ³ CH ₄ 100 mg/m ³ CH ₄	–

^aInstallation with a catalyst.

^bAdmissible limit at the inlet of an adsorber with active coal.

Both the components of escaping biogas and products of its combustion release to atmosphere, causing toxicological and unpleasant smell effects. Some of these compounds, especially chlorinated hydrocarbons, demonstrate carcinogenic action. Chlorine in biogas may cause, when its combustion runs under unfavourable conditions, emission of dioxines and furanes. Due to aforementioned reasons, it is especially important to control both individual selected compounds of S, Cl and F, and also their total content levels. Review of limiting concentrations for S, Cl and F compounds existing in biogas is given in the Table.

3. MATERIALS AND METHODS

Due to the immense number and diversity of S, Cl and F compounds present in biogas, it is impossible in practice to determine their sum based on the concentration

measurements for individual constituents. In the case of measurements of total sulfur compounds, two groups of potentially suitable methods can be distinguished: hydrogenation of sulfur compounds and measurement of generated H_2S , and combustion of sulfur compounds with determination of generated SO_2 . The combustion method can also be successfully applied to determine a total level of chlorine and fluorine compounds. The idea of this method consists in oxidizing S, Cl and F compounds to SO_2 , HCl and HF, respectively, absorbing selectively these compounds and determining them by well-known analytical methods.

Determination of SO_2 was made using the spectrophotometric method [11], selective and neutral with respect to other components of biogas. The method consisted in SO_2 absorption in solution of sodium tetrachloromercurate and spectrophotometric analysis of the obtained complex. To determine HCl and HF, products of combustion of biogas were absorbed in deionised water and the post-sorption solution was analyzed for Cl^- and F^- ions using an ionic chromatograph with a conductometric detector and an anionic column.

A basic element of the research system (Fig. 1) is a furnace for flameless combustion of biogas (Fig. 2) equipped with a quartz tube installed inside a corundum tube around which a heating element (11), in a form of kanthal resistance wire, was wound. The quartz tube was ground on its both ends, the inlet polished section was used to connect glass head of the burner (9), while the outlet one – to connect the glass cooler (12). Two thermoelements, NiCr–Ni (10), installed between the two tubes, were used to monitor and control the combustion temperature. The voltage was adjusted using a laboratory type control transformer (20). Resistance wire was supplied via a contactor (19) controlled by a microprocessor based temperature recorder/controller (14). The recorder received voltage signal from a thermoelement installed close to the point where biogas was introduced into the quartz tube. Additionally, a digital millivoltmeter (15) was used to record temperature measured by another thermoelement located at the furnace outlet. Immediately before and after the measurement, the temperature inside the quartz tube was taken manually using the same type of thermoelements. The furnace was insulated using 150 mm thick thermoinsulating quartz wool with the thermal resistance of 1430 °C and the whole unit was housed in a duralumin sheet.

Combustion air was fed into the furnace via a rotameter (5), a column with acid compound sorbent (7) and a column with active carbon (8). The furnace was fed with biogas from receivers (6) using purity class 5.0 nitrogen supplied from a cylinder (2), via a pressure regulator (3), a flexible Tedlar bag (4) and a rotameter (5). Biogas and nitrogen were introduced into the furnace via a nozzle installed in the inlet head (9) where they contacted with air oxygen within the zone of temperature of 1200 °C. The air was fed so as to ensure turbulent conditions of media mixing while preset volumetric streams of air and biogas and their proportions ensured safe and stable conditions of flameless combustion in the quartz tube and relatively long time of contact exceeding 7 s. Such conditions of combustion gave full oxidation of S, Cl and F compounds.

Combustion products, after cooling down on a glass connecting member (12) to ca. 60 °C, (i.e., 20–30 °C above the flue gas dew point controlled with a thermometer (13)), were directed to a set of aspiration washers (16), and then subject to analysing with a spectrophotometer (21) or an ion chromatograph (22). An automatic aspirator (18) equipped with a silica gel gas dryer (17) was used to ensure flow of media, regulation and recording of the volumetric flow rate.

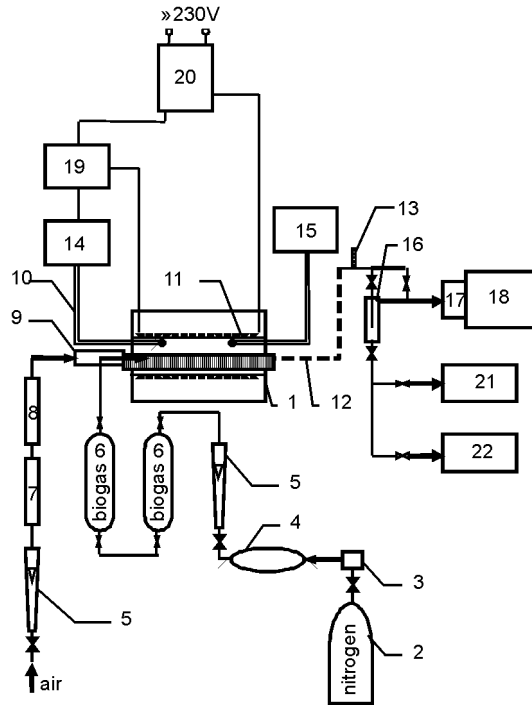


Fig. 1. Schematic diagram of the laboratory plant: 1 – furnace, 2 – cylinder with compressed nitrogen, 3 – pressure regulator, 4 – flexible Tedlar bag, 5 – rotameter, 6 – gas receivers, 7 – column with active carbon, 8 – adsorber of acid compounds, 9 – inlet head, 10 – thermoelement, 11 – heating element, 12 – cooler, 13 – thermometer, 14 – temperature controller and recorder, 15 – millivoltmeter, 16 – gas washers, 17 – gas dryer, 18 – aspirator, 19 – electronic transmitter, 20 – laboratory autotransformer, 21 – spectrophotometer, 22 – ion chromatograph

Prior to measurements, the biogas pressure in receivers was made equal to the atmospheric pressure; receivers, air purifying columns and washer set were connected and the furnace was pre-heated to a specific temperature. Total volume of biogas sample was dependent on hydrogen sulfide concentration, which was measured, along with biogas flow, using spectrophotometric method [12]. When temperature inside the furnace was as required, in order to rinse out the system and to heat up the glass connecting member, the aspirator was turned on (with air inlet being opened, nitrogen and biogas inlet closed

and washer by-pass opened), and then – after temperatures become stable – the by-pass was closed, flow through washers was opened, nitrogen flow was enabled, valves and biogas receivers were made open and streams of media were adjusted so as the air flow rate was 40–50 dm³/h, and nitrogen flow rate about 1 dm³/h. Then, in 20 min periods, the nitrogen flow rate was increased to 2, 6 and 12 dm³/h, respectively. Measurement was terminated when receivers were washed out at least 10 times.

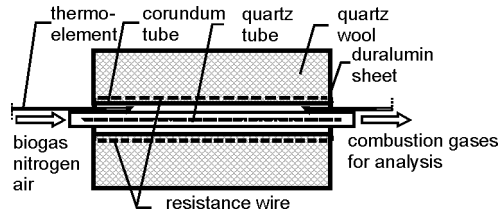


Fig. 2. Schematic diagram of biogas flameless combustion furnace

An exemplary combustion time for biogas sample of 5 dm³ was about 7 h. Post-sorption solutions from washers were analyzed for SO₂, HCl and HF content, and on the grounds of these data the calculations were made for the total content of elements under investigation in the biogas.

4. RESULTS

Fig. 3 shows biogas testing results for the content of total sulfur, chlorine and fluorine get by the aforementioned method, and – for comparison purposes – the results of

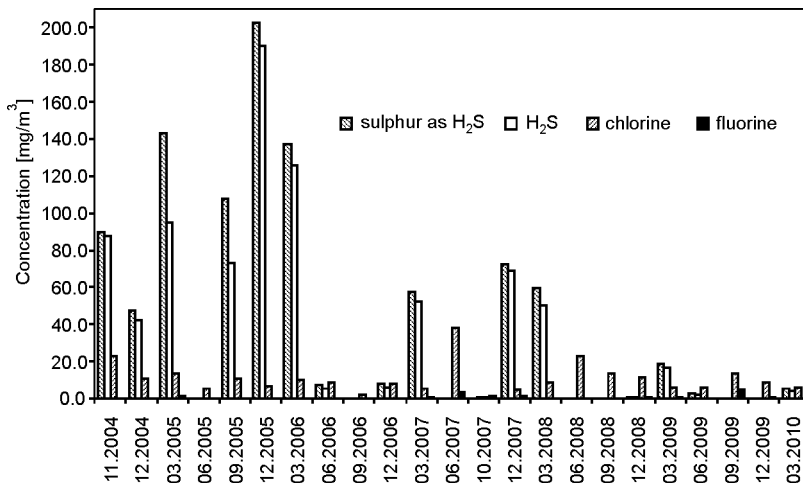


Fig. 3. Concentrations of selected biogas constituents sampled at the inlet of an electric generator gas engine

parallel measurements of H₂S concentrations by the spectrophotometric method. The research was made for biogas, purified by bog ore and active carbon adsorbers, fed into two gas engines of generators with the rated electric power of 601 kW each. The results are averaged values for the two parallel generators, recalculated to standard conditions (273K, 101.3 kPa) and to dry gas.

5. SUMMARY

The proposed method to determine total content of sulfur, chlorine and fluorine compounds in biogas is free of disadvantages of numerous methods being in use. Its most important advantages are as follows: determination of all three elements could be made in a single unit, low cost of system construction, elimination of usage of hydrogen and oxygen, safety of operation, full automatic control over combustion temperature due to application of an electrically heated tube and relevant automation, initiating the combustion process without need to dismount the burner etc. The key matter for the effect of research (i.e. full oxidation of S, Cl and F compounds) was to establish the optimum combustion temperature and reliable temperature of monitoring and automatic control. Examinations allowed one to establish the ratio volumetric flows of air to biogas providing sufficiently long contact time of reagents and combustion conditions eliminating the risk of explosion.

The method was tested and verified in multiple biogas measurements made in 2004–2010 in one of Polish municipal sewage treatment plants. The results of examinations allowed one to determine the range of concentrations for hydrogen sulfide sulfur, total sulfur and total content of chlorine and fluorine compounds in typical biogas generated from sludge digestion and to evaluate average fraction of hydrogen sulfide sulfur in total sulfur. It was proved that this fraction may vary from 66% to 98% with the average value of 83%. Thereby, it was confirmed that periodical determination of total sulfur, apart from determining hydrogen sulfide in biogas which is routinely run in sewage treatment plants, is both justified and necessary.

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EMISSION OF VOLATILE ORGANIC COMPOUNDS FROM DIESEL ENGINE FUELLED WITH OIL–WATER EMULSIONS

Exhaust gas from compression ignition engine fed with oil–water emulsions containing 10 vol. % of water or H₂O₂ (30 vol. %) water solution in commercial diesel oil have been analysed and the results compared with the composition of flue gas when diesel oil alone was used. The analyses concerned concentrations of NO, total NO_x, carbon monoxide, the sum of hydrocarbons as well as volatile organic compounds. When emulsion was used, considerable reduction of nitrogen oxides (however for low engine load only) and slightly lower smokiness of flue gas was reached; on the other hand, it caused higher concentrations of CO, aromatic hydrocarbons and the highest increase, even up to 10-fold, of acetaldehyde concentration, a typical product of incomplete combustion of organic compounds.

1. INTRODUCTION

Continuous increase in the number of motor vehicles and the distances travelled are observed all over the world and their growth rate seems unpredictable. In particular, the number of automotive vehicles increases very rapidly in the Far East countries, China or India, due to their technological boom. Also in Poland, the number of registered vehicles has distinctly increased compared with previous years (Table 1) [1].

Conventional fuels, including petrol and diesel oil, are mixtures of various hydrocarbons. As an effect of their complete combustion under ideal conditions, both in spark-ignition engines fuelled with petrol and in compression ignition engines fed with diesel oil, just harmless compounds, like CO₂ and water, should be generated. In practice, this type of combustion never occurs and like in all combustion processes of hydrocarbon fuels, a whole series of air pollutants can be found in flue gas – carbon

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monoxide, hydrocarbons, and among them especially dangerous polycyclic aromatic hydrocarbons (PAHs), nitrogen oxides, sulfur oxides and particulate matter (PM). Motor vehicles are responsible for significant fraction of total emission, first and foremost the nitrogen oxides (38.5%), carbon monoxide (22%), and, to a slightly lower extent, non-methane volatile organic compounds (16%) [1].

Table 1

Number of recorded vehicles in selected sectors

Sector	Year			
	1970	1990	2000	2007
Motor cars	479 000	5 261 000	9 991 000	14 589 000
Trucks	274 000	1 045 000	1 879 000	2 521 000
Buses	78 000	80 000	82 000	88 000

Pollutant emission depends on the fuel type and the way it is combusted in an engine. In the case of compression ignition engines fed with diesel oil where combustion always takes place with large excess air, the main problem consists in emission of nitrogen oxides and smoke – specific diesel particulate matter (PM), so called “diesel soot”. Diesel PM consists of insoluble material – particles of condensed carbonaceous material with ash from the engine oil and fuel additives, adsorbed water, sulfur compounds (sulfuric acid or sulfates) and adsorbed soluble organic fraction (SOF), which is a complicated mixture of organic compounds, including both volatile organic compounds (VOCs) and PAHs, soluble in methylene chloride.

Pollutant emission of vehicles can be reduced with primary methods which lead to improve the conditions of fuel combustion (to burn less fuel and more efficient) by optimisation of engine construction and the whole fuel supply system. Another solution is to use unconventional drives (e.g. electric or hybrid) and fuels. Most often it refers to biofuels, e.g. esters of plant origin fatty acids (fatty acid methyl esters – FAME) having been added in various proportions to diesel oil. Mixtures of diesel oil and esters allow one to reduce pollutant emission, first of all the PM (by 20–50%), carbon monoxide (11–25%) and hydrocarbons (20–32%), however the NO_x emission may increase [2, 3].

Another proposal consists in feeding diesel engines with oil–water emulsions where water droplets are surrounded by film of liquid fuel. High temperature existing in combustion chamber causes evaporation – at first of water and then of the fuel. Evaporating water supports atomizing of fuel droplets which favours full combustion of fuel at somewhat lower temperature. As an effect of emulsion combustion, the concentration of basic pollutants in flue gas, i.e. diesel soot and nitrogen oxides, are reduced. Oil–water emulsions properties depend on water volume fraction in fuel. In practice, it is up to 30%. Elf Company’s fuel, brand name Aquazole, including about 13% of water and 2% of stabilizing additives in low-sulfur diesel oil, ensures NO_x

reduction by 15–30% and soot by 10–50%. At the same time, engine power reduces by about 4% and fuel consumption rises by 10–15% as compared with diesel oil alone [4]. In any way the concentrations of CO and organic compounds can increase [5].

The purpose of the work was to compare chemical compositions of exhaust gases of diesel engine fuelled with pure commercial diesel oil and those of oil–water emulsions containing 10 vol. % of distilled water or the same content of 30% water solution of H₂O₂.

2. EXPERIMENTAL

Tests were carried out with a diesel engine S301D with a hydraulic load brake HWZ1 equipped with an extensometer force transmitter with accessories allowing one to measure and to control operating parameters of the engine. In order to simulate characteristic standard mode of driving, examinations were performed for three rotational speed values of engine crankshaft, 1200, 1400 and 1600 rpm and two levels of engine torque (*Mo*) of 10.72 and 21.28 N·m. Measurements were taken for the following operating points of the engine:

- 1) $n = 1200$ rpm, $Mo = 10.72$ N·m
- 2) $n = 1200$ rpm, $Mo = 21.28$ N·m
- 3) $n = 1400$ rpm, $Mo = 10.72$ N·m
- 4) $n = 1400$ rpm, $Mo = 21.28$ N·m
- 5) $n = 1600$ rpm, $Mo = 10.72$ N·m
- 6) $n = 1600$ rpm, $Mo = 21.28$ N·m

Apart from commercial diesel oil for summer season (ON), two oil-water emulsions were prepared, one with 10 vol. % of distilled water in ON (ON+) and one with 10 vol. % of 30 vol. % H₂O₂ solution (ON++). Emulsions were prepared in the Institute of Machine Construction and Operation, Wrocław University of Technology using ultrasonic washer.

2.1. ANALYTICAL MEASUREMENTS

Concentration of formaldehyde was determined by the colorimetric method, according to Polish Standard PN-71/C-04593, after absorbing the aldehyde in water. The remaining VOCs were adsorbed on active carbon and, after desorption with CS₂, they were analyzed with gas chromatograph, using a Hewlett-Packard HP 5890 Series II apparatus, with a FID detector and a HP PONA capillary column (50 m long with stationary phase film 0.5 μm thick). Exhaust samples were taken from the outlet system via a probe. The gas was split into two streams – formaldehyde was absorbed in

washers containing 10 cm³ of distilled water, VOCs were adsorbed and concentrated on active carbon. Samples were taken simultaneously using a two-channel aspirator. Flow rates of flue gases in each system were 20 dm³/h and the sampling time was 30 min. A scheme of the testing stand is shown in Fig. 1.

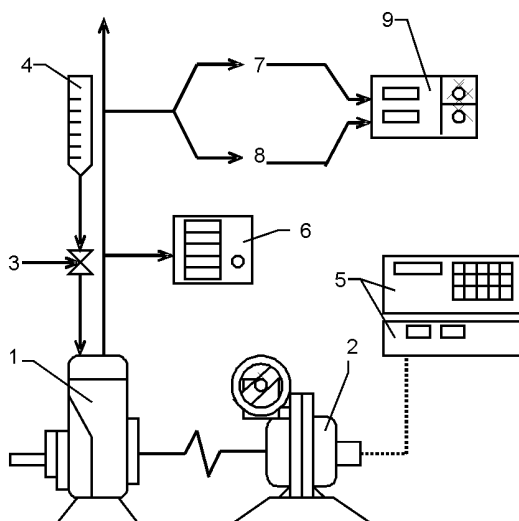


Fig. 1. Scheme of testing stand: 1 – engine, 2 – load brake, 3 – fuel supply, 4 – test fuel supply system, 5 – rotational speed and torque meters, 6 – flue gas analyzers, 7 – absorbing washer, 8 – pipe with adsorbent (active carbon), 9 – two-channel aspirator

3. RESULTS AND DISCUSSION

Experiments by the gas chromatographic method revealed a series of compounds, of which those of the biggest chromatographic peaks were determined qualitatively and quantitatively. Within the group of aldehydes, apart from formaldehyde determined by the colorimetric method, exhaust gas contained acetaldehyde, propanal and acrolein, alcohols (amyl, *n*-butyl and isobutyl), methyl isobutyl ketone, aromatic hydrocarbons (benzene, toluene, xylene) and alkanes (heptane, octane, decane).

The concentrations of aromatic hydrocarbons (AHC), aldehydes and other compounds determined for the specific working points of the engine are shown in Fig. 2.

When diesel oil alone was used, higher concentrations of aromatic hydrocarbons were observed for the higher load of engine, and – independently of its rotational speed – they amounted to about 0.25 g/m³. At this engine load, combustion of oil–water emulsion produced somewhat lower concentrations of AHC but serious, almost twofold rise of the concentration of these compounds took place during combustion of oil–perhydrol emulsion, especially at the engine test points 2, 3 and 4.

When engine was fuelled with diesel oil only, the concentrations of aldehydes, except series 3, were slightly lower than that of AHC and amounted to 0.1 g/m^3 . Combustion of both emulsions caused a considerable higher concentration of aldehydes than during oil combustion; especially at the lowest rotational engine speed of 1200 rpm they were almost 8-fold and over 10-fold higher for the lower and higher engine load, respectively. Such result is particularly dangerous – aldehydes are recognized as strongly irritating compounds for human being and on the other hand for their great potential to create photochemical smog with nitrogen oxides.

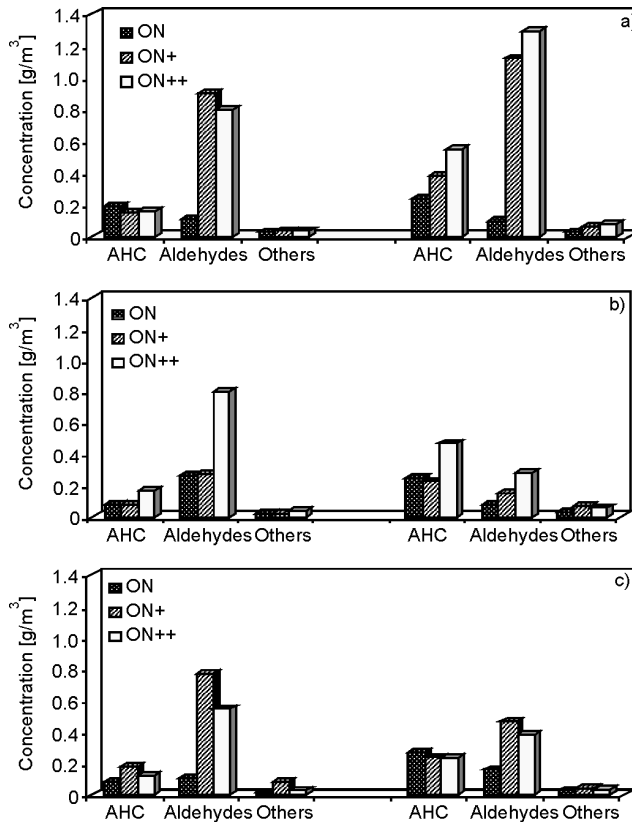


Fig. 2. Total concentrations of aromatic hydrocarbons (AHC), aldehydes and other identified organic compounds (alkanes, ketones and alcohols) depending on the fuel combusted, at the rotational speed of: a) 1200 rpm, b) 1400 rpm, c) 1600 rpm; $M_o = 10.72 \text{ N}\cdot\text{m}$ – on the left-hand side, $M_o = 21.28 \text{ N}\cdot\text{m}$ – on the right-hand side

The part of remaining organic compounds in total VOCs emission was much lower but also in this group higher concentrations of organic compounds were observed when the both emulsions were combusted than when diesel oil only was used.

Among hydrocarbons, benzene occurred in the highest concentrations (maximum 0.126 g/m^3). Its concentration increased with increasing both load and rotational speed of engine. Similar trend of concentration changes was observed for the remaining AHC, however their concentrations were substantially lower and reached 0.11 and 0.037 g/m^3 only for xylene and toluene, respectively. Much lower concentrations, at least two orders of magnitude with respect to benzene, occurred for alkanes and they were similar for all compounds determined.

In the group of oxy-derivative compounds, aldehydes were determined in the highest concentrations and among them, acetaldehyde, typical product of incomplete combustion of VOCs representing organic compounds of various chemical structure [7–9]. The concentration of acetaldehyde varied within 0.03 to 0.063 g/m^3 . Concentrations of other determined aldehydes were lower and amounted about 0.04 g/m^3 , 0.03 g/m^3 and 0.02 g/m^3 for propionaldehyde, acrolein and formaldehyde, respectively. Concentrations of remaining oxy-derivative compounds were much lower and did not exceed 0.007 g/m^3 . Both these compounds – benzene and acetaldehyde are particularly hazardous – which is proved by very stringent their maximum available concentrations in air (Table 2).

Table 2

Maximum available concentrations of selected compounds in air [9]

Compound	Classification (No. CAS)	Maximum available concentration [$\mu\text{g/m}^3$]	
		1 hour	Year
Benzene	71-43-2	30	5
Acetaldehyde	75-07-0	20	2.5

As was shown above, combustion of both emulsions increased the concentration of VOCs; the same tendency was observed for benzene and acetaldehyde. The concentrations of those compounds, depending on the fuel combusted, are presented in Figs. 3 and 4.

Benzene concentrations for all tests were lower at a lower rotational speed and load of engine. When oil alone was combusted, benzene concentrations at $Mo = 10.72 \text{ N}\cdot\text{m}$ lowered from 0.054 to 0.032 g/m^3 for 1200 and 1600 rpm, respectively. Oil combustion at a higher engine torque ($Mo = 21.28 \text{ N}\cdot\text{m}$) resulted in distinctly (2–4-fold) increase of benzene concentration in the waste gases, amounting to 0.125 g/m^3 . Combustion of both emulsions, particularly the oil–perhydrol emulsion, brought the increase of benzene concentrations, practically at each point of the engine test, amounting to maximum value of 0.242 g/m^3 at the test point 2.

For combustion of diesel oil at each test point, the concentration of acetaldehyde in the exhaust gases changed within 0.024 – 0.062 g/m^3 . Similar was the concentration of propanal. Formaldehyde and acrolein were detected in much lower concentrations

(0.008–0.024 g/m³). Engine fuelled with both emulsion produced slightly more acetaldehyde – its concentration increased even 20–30-fold, exceeding the value of 1 g/m³.

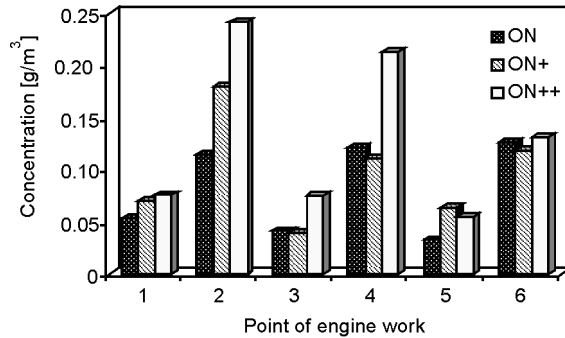


Fig. 3. Concentration of benzene in waste gases during fuels tested combustion

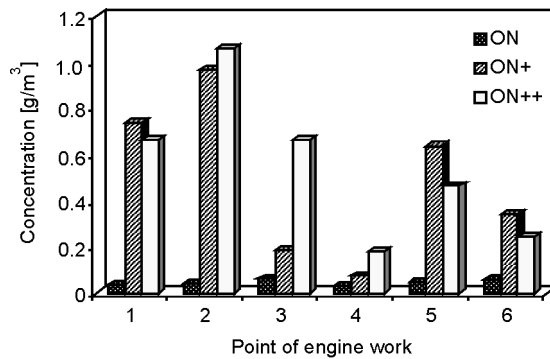


Fig. 4. Concentration of acetaldehyde in waste gases during fuels tested combustion

Combustion of oil–water emulsion probably contributes to deterioration of combustion parameters in terms of the abatement of local combustion temperature and additional oxygen atom, contained in water molecule enabled incomplete oxidation of fuel hydrocarbons to acetaldehyde only. On the other hand, when both emulsions were combusted, only formaldehyde was produced in lower concentrations at every engine test point, than when oil alone was burnt.

4. CONCLUSIONS

Combusting of oil–water emulsions leads to reduced emission of the most important air pollutants generated by compression ignition engines – nitrogen oxides and

diesel soot [10]. However, it also contributes to higher concentrations of volatile organic compounds in flue gas, including dangerous aromatic hydrocarbons or aldehydes. Despite improved degree of fuel dispersion in oil–water emulsions, combustion of organic compounds originating from oil may be inhibited by the presence of water – ballast decreasing local temperature of combustion. It should be emphasized that tests were made using an old-design engine and, under such conditions, complications with combustion of a fuel other than diesel oil are more evidently highlighted.

Oil–water emulsions can be successfully applied to any direct injection diesel engine without engine construction or settings changes. Fundamental disadvantage of this fuel is a low durability of such emulsions. Special additives are necessary to be used, so-called emulsifiers, reducing the surface tension, and in this way enhancing fuel durability. At present, oil–water emulsions are used seldom, mainly as fuels for municipal buses in some towns in France or USA.

The performed tests on the combustion of oil–water emulsions showed potential for decrease of emission of some groups of air pollutants, mainly NO_x and soot, however complex systems of flue gas treatment need to be used to reduce the emission of all air pollutants such as carbon monoxide and volatile organic compounds which can be easily oxidized in catalytic reactions.

For the fact that application of emulsions can decrease concentrations of the most dangerous air pollutants generated by diesel engines, research work on combustion of such emulsions should be surely continued.

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EMISSION FROM STATIONARY COMBUSTION SOURCES AS THE DETERMINANT OF ENERGY AIR QUALITY INDEX

The energy air quality index (EAQI) is proposed as an essential criterion for evaluation of air quality in urban areas. EAQI connect the air quality with the structure of energy consumption and with conditions of emission resulting from urban development structure. The method of determination of EQAI connected with stationary combustion sources, along with defining the toxicity equivalents of emitted pollution, has been presented. Classification specifying potential threat to air quality based on the EQAI value is hereby proposed and an example of calculation the index value for a real urban area is shown.

1. INTRODUCTION

Air quality in urban areas is influenced by natural and anthropogenic factors. There exists a possibility for improvement of air quality through shaping the latter. Urban complex is a concentrated recipient of direct energy. It is assumed that for an urban complex, without essential participation of onerous industry and insignificant (in the general balance) value of flow of pollution from outside of the complex, the most essential anthropogenic factor with dynamic influence on air quality is combusting fuels in stationary and mobile sources. An important anthropogenic factor with static influence on the air quality is the urban structure. That is why energetic and ecological analyses of combusting sources and processes, consistent with the principle of sustainable development, should be a vital element of evaluation of air quality. Such approach to the subject, even though it should relate to the whole urban complex, is particularly foreordained to areas characterised by dense residential quarters with a considerable number of individual stationary combustion sources and with admitted combustion engine vehicle traffic.

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2. METHOD OF CALCULATION OF THE ENERGY AIR QUALITY INDEX

2.1. DEFINITION OF THE ENERGY AIR QUALITY INDEX

The energy air quality index (EAQI) is proposed as an essential criterion for evaluation of air quality in an urban area. EAQI is defined by equation connecting air quality with structure of energy consumption and with emission conditions resulting from buildings structure:

$$EAQI = EAQI_s + EAQI_t = E_{sFR}Y_{WH} + E_{tFR}Y_{WC} \quad (1)$$

The coefficients Y_{WH} , Y_{WC} as well as E_{sFR} are defined in Eqs. (6), (10), (12). The coefficients: \bar{W}_{EEUA} (Eq. (7)) and W_{Qd} (Eq. (8)) are adopted as additional criteria. Separate determining of the values of $EAQI_s$ (connected with stationary emission sources) and $EAQI_t$ (connected with traffic emission sources) allows a detailed analysis of factors influencing the air quality.

Based on the results of analyses of six hypothetical urban areas with homogeneous heat supply structure [1–3], a classification of air quality has been proposed (Table 1) for determining potential threat based on the $EAQI_s$ values.

Table 1

Air quality dependent on the $EAQI_s$ value

EAQI _s [mg/(m ² ·h)]	Air quality
0–400	1 – very good
401–1500	2 – good
1501–3500	3 – moderate
3501–6000	4 – unhealthy
Above 6000	5 – hazardous

EAQI does not take into account meteorological phenomena as independent of humans. Neither does it take into account the wind direction and its velocity, as in the areas of compact settlement considerable fluctuations of these parameters occur with general velocity reduction. Due to great variances of concentrations of species in the areas behind buildings and in street canyons, the values of E_{sFE} and E_{tFE} are approximated in time and space.

2.2. DETERMINING THE SURFACE AREA STRENGTH FOR A POLLUTANT EMITTED FROM STATIONARY ENERGY LOW SOURCES

Calculation of the E_{sFE} coefficient based on the structure of heat supply and values of W_{Qd} and \bar{W}_{EEUA} comprises the following steps:

1. Determining of the usable energy value Q_{us} for recipients (buildings) along with defining its components and the direct energy value Q_d .
2. Determining of the primary energy value Q_p for these components of Q_{us} for which energy is consumed in the analyzed area (or adjacent areas).
3. Calculation of the factor of the local energy costs of the energy supply structure for the analyzed area according to the dependence:

$$W_{QUA} = \frac{Q_{pUA}}{Q_{us}} \quad (2)$$

3a. If all energy sources (heat and electrical energy both for living and technological needs) are beyond the area or if they have high stack, then:

$$W_{QUA} = 0$$

which means that the urban strength for a pollutant emitted from stationary (point) energy sources

$$E_{sFE} = 0$$

and the only emission from the buildings is anthropogenic heat emission:

$$W_{Qd} > 0$$

3b. In the case of heat supply structure totally based on local heating and (or) boiler houses with short stacks

$$W_{QUA} > 1 \text{ GJ}_p/\text{GJ}_{us} \quad \text{and} \quad E_{sFE} > 0$$

generally

$$W_{QUA} = (1.1 - 1.8) \text{ GJ}_p/\text{GJ}_{us}$$

4. Calculation of the value of the emission of i -th species from the analyzed area, for each of n components of Q_{us} , connected with Q_p consumption, and based on defined factors of pollution emission for heat supply structures W_{Ei}

$$E_{iUA} = \sum (Q_{us} W_{EiUA})_n \quad (3)$$

where the emission E_{iUA} concerns fuels combusted in sources situated in the analyzed area.

5. Calculation of the equivalent pollution emission rate based on the defined toxicity equivalents k_{Ui} of the analyzed pollution (Sect. 2.4):

$$E_{EUA} = \sum (k_{Ui} E_{iUA}) \quad (4)$$

6. Calculation of the strength on the surface area F_U for a pollutant i emitted from low stationary energy sources:

$$E_{sFi} = \frac{E_{iUA}}{F_{UA}} \quad (5)$$

and equivalent emission rate from low stationary energy sources:

$$E_{sFE} = \frac{E_{sEUA}}{F_{UA}} \quad (6)$$

7. Calculation, of the cost coefficient of the ecological energy supply, an average for the analyzed area, which takes into account the equivalent pollution load E_{sEUA}

$$\bar{W}_{EEUA} = \frac{E_{sEUA}}{Q_{us}} \quad (7)$$

8. Calculation of the strength of the urban area for a direct energy consumption Q_d

$$W_{Qd} = \frac{Q_{dUA}}{F_{UA}} \quad (8)$$

2.3. FACTORS TAKING INTO ACCOUNT EMISSION CONDITIONS IN A URBAN STRUCTURE

Complexity of urban systems as well as variety of architectural structures do not allow complete consideration of their influence on substance dispersion, especially in the compact settlement areas. The purpose of introducing the urban factors to EAQI formula is to take into account relative deterioration of the dispersion conditions of emitted pollution, as an outcome of unfavourable technical conditions of emission.

The factor of technical conditions of emission W_H and the street canyon factor W_C were considered particularly important:

1. Factor of technical conditions of emission W_H

$$W_H = \frac{h_s}{H_{Bav}} \quad (9)$$

is the ratio of the emitter height h_s to the average height of residential buildings H_{Bav} in the range of cavity region of a building, that is up to $x = 6H_B$. The value $W_H < 2.0$ (2.5) characterizes low emitters. The W_H factor for an analyzed area is determined as the weighted average with respect to the equivalent emission rate from short stacks.

An average value of Y_{WH} for $W_H = 1$ was determined based on experimental investigations of the author [1]. The value Y_{WH} for $1 < W_H < 2.5$ was determined based on Elterman's dependence [4] with concentrations of emission for low stacks [5, 6]. Dependence of the EAQI_s value on the W_H factor for $1 \leq W_H < 2.5$ is given by the following equation:

$$Y_{WH} = \frac{\bar{C}}{C_{WH=2.5}} = 70.9 \exp(-1.72W_H) \quad (10)$$

From the equation, the average value of the relative concentration of a species in the area of aerodynamic cavity region may be estimated on the leeward side of building, in a vertically limited space: by leeward wall and surface $x = 5H_B$, and horizontally by surfaces $z = 0.1H_B$ and $z = 0.4H_B$. It has been assumed that it is a space, where people are especially vulnerable to emission from low point sources. The concentration reference point $C_{WH=2.5}$ is the pollutant concentration in the described space when $h_s = 2.5H_B$, i.e. when the stack can be treated as a high one.

2. Street canyon factor W_C :

$$W_C = \frac{H_{Bav}}{W} \quad (11)$$

is the ratio of the average height of buildings delimiting the canyon at the length $L > 2.5H_B$ to the total width of the street W . Depending on its value, three types of flow, perpendicular to the canyon symmetry axis, can be classified [7, 8]:

- skimming flow, for $W_C > 0.9$, is characterized by significant reduction of air exchange inside the canyon,
- wake interference flow, for W_C from 0.30 to 0.9, when alongside stream circulation inside the canyon, cleansing of a part of pollution and transporting it (mainly within the wake region) to adjacent canyons exists,
- isolated roughness flow, for $W_C < 0.30$, when the influence of reciprocal interaction of the canyon walls on the flow interference can be ignored.

The value of W_C factor has a decisive influence on diffusion of pollution from traffic sources but also from adjacent low stationary sources [9, 10].

Based on the investigations of Chang et al. [10] and Sini et al. [11] an equation determining the dependence of the $EAQI_t$ value on W_C has been developed:

$$Y_{WC} = \frac{C}{C_{WC=0.25}} = 0.7 \exp(1.3W_C) \quad (12)$$

with the following boundary conditions:

- a) for $W_C > 0.9$, $Y_{WK} = 2.5$ – skimming flow,
- b) for $0.30 > W_C > 0.9$ – wake interference flow
- c) for $W_C < 0.3$, $Y_{WC} = 1.0$ – isolated roughness flow – $EAQI_m$ does not depend on W_C .

Based on Eq. (12) an average value of relative concentration in the region of leeward wall may be estimated, horizontally restricted by planes $z = 0.1H_B$ and $z = 0.4H_B$. Concentration reference point is pollutant concentration in the area under investigation for $H_{Bav} = 0.25W$, i.e. when the influence of a canyon can be neglected.

2.4. TOXICITY EQUIVALENTS OF EMITTED POLLUTANTS IN EVALUATION OF AIR QUALITY

Toxicity equivalents of emitted pollutants k_{U_i} , with regards to the reference substance, are determined for primary pollution taking into account the following factors:

- direct influence of the pollutant on living organisms (especially on humans),
- the range of pollutant interaction also with various components of the environment,
- life span of emitted pollutant,
- physicochemical processes involving the pollutant,
- secondary impacts arising from pollution.

The toxicity equivalents thus differ from the toxicity coefficients which are determined based on ambient air quality standards.

Values defined in the Life Cycle Assessment (LCA) procedures have been accepted as the basis for determining the toxicity equivalents of pollutants emitted from combustion processes. They concern pollution emission and take into account the factors listed. The following categories of environmental impacts have been selected [12]:

- human toxicity potential (HTP),
- photochemical ozone creation potential (POCP).

The following ambient air quality standards were also analyzed:

- permissible concentration of pollutants in EC with regards to human health [13],
- air quality standards according to NAAQS, US EPA [14],
- air quality standards according to WHO [15],
- air quality standards according to NAAQOs, Canada [16],
- permissible concentration of air pollutants in Poland [17].

Sulphur dioxide SO_2 is (traditionally) assumed the reference. Other references in the LCA procedure are also used (3,4 dichlorobenzene for HTP, ethylene for POCP). This fact was taken into consideration. The method of calculation of toxicity equivalents for analysed pollutants has been presented elsewhere [1].

The value of k_U has also been calculated for CO_2 as pollution which, due to the magnitude of emission from burning processes, influence air quality in areas with restricted diffusion. As the basis for determination of the toxicity equivalent of CO_2 with respect to SO_2 , their concentrations in the air of medium sized cities (according to European Standard for Ventilation EN 13779) have been assumed. The determined values of k_{U_i} are given in Table 2.

Table 2

Toxicity equivalents of emitted pollutants k_{U_i}

Pollutant	SO_2	NO_2	CO	PM_{10}	benzene	VOC	CO_2
Equivalent k_{U_i}	1	8.5	0.25	8.3	75	5.0	$1.5 \cdot 10^{-5}$

3. AN EXAMPLE OF DETERMINING OF THE $EAQI_s$ VALUE (CONNECTED WITH STATIONARY EMISSION SOURCES) FOR REAL URBAN AREAS

Based on the stocktaking of stationary emission sources connected with covering of energetic demand and those of heat energy recipients in Jeżyce district in Poznań [18], the $EAQI_s$ was determined taking into consideration low stationary sources for real conditions. The analyzed district of the surface area of $F = 4\,028\,000\text{ m}^2$ was divided into nine areas of similar urban structure. The analysis comprises the regions:

- with compact settlement (from the beginning of the 20th century) with significant contribution of individual heating (coal, gas, electric energy) and built-in boiler houses (regions: A2A, A2C, A2D),
- with multi-family apartment building development (from various periods of the second half of the 20th century) with built-in boiler houses, either local or supplied by city heating network (regions: A2B, A2E, C11A, C11C),
- with detached single family development with green areas, with built-in boiler houses (regions: C11B, C11D).

Next to the residential buildings there are also administrative, educational, commercial, service and manufacturing facilities in the district. Stacks of individual heaters and boiler houses are short what compared to W_{Hav} values (Table 4).

In accordance with the method presented in Sect. 2.2, energetic and ecologic factors defining $EAQI_s$ have been assigned to individual subareas. The analysis was conducted for average climate conditions of three winter months with the lowest outside temperature (December, January, February), related to 60 min. The results are shown in Figs. 1–3 and Tables 3 and 4.

The analyzed part of the city is diversified both in terms of urban development and structure of energy consumption. Values of the local energy costs $W_{QUA} > 1$ (Fig. 1, Table 4) point to a dominant contribution of individual heating and built-in boiler houses. This pertains to sub areas A2D, C11B, and C11D. Contribution of these sources is also relatively large ($W_{QUA} = 0.75$) in the sub area A2C. The values of the ecological costs coefficient W_{EEUA} (Table 4) result from properties of fuel, being energy carriers. Large values W_{EEUA} of in the sub areas A2D, C11B, A2C, and C11D indicate a dominant or significant contribution of coal as a fuel.

$EAQI_s$ values which take into account not only energetic and ecological costs but also the concentration of sources, along with urban structure, point to the potential occurrence of given states of air quality. A specific case is the subarea A2D (Fig. 3, Table 4) for which $EAQI_s = 4698\text{ mg}/(\text{m}^2\cdot\text{h})$, belonging to the „unhealthy class” of air quality (Table 1). The causes for this state, apart from high W_{QUA} and W_{EEUA} coefficients, are compact settlement and small values of W_{Hav} (Table 4). Dense building development and high W_{QUA} and W_{EEUA} coefficients are the reason for classifying subareas A2A and A2C to the third class of air quality (moderate). Sub areas C11B and C11D, despite large W_{QUA} and W_{EEUA} coefficients, are ranked as follows:

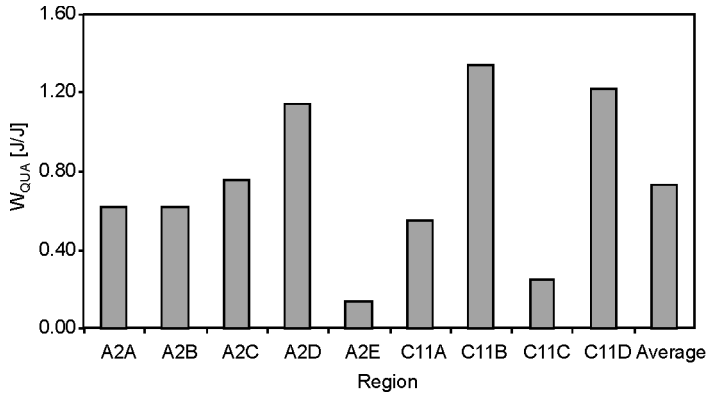


Fig. 1. Factors of energy costs of the energy supply structure W_{QUA} for the sub areas

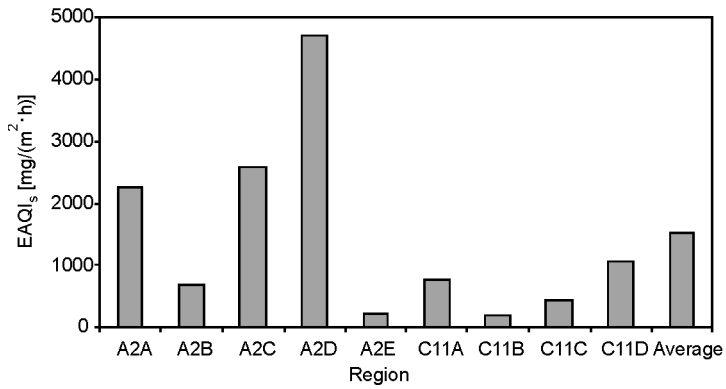


Fig. 2. Values of Energy Air Quality Index EAQI_s for sub areas

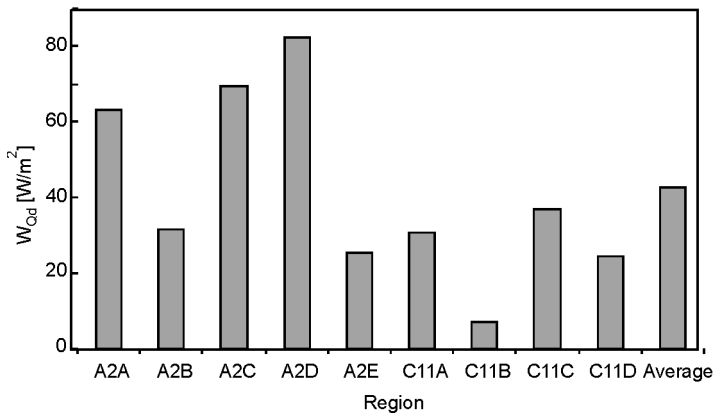


Fig. 3. The sub urban areas strength for direct energy consumption W_{Qd}

Table 3

Pollution emission from stationary energy sources for the analyzed regions

Region	Area F_U [m ² ×10 ³]	E_s						E_{sEUA} [kg/h]
		SO ₂ [kg/h]	NO ₂ [kg/h]	PM ₁₀ [kg/h]	CO [kg/h]	VOC [kg/h]	CO ₂ [Mg/h]	
A2A	419	10.79	2.08	5.89	10.30	2.44	3.47	92.20
A2B	553	3.11	1.70	1.67	3.16	0.76	2.23	36.09
A2C	425	15.55	2.59	8.53	14.82	3.48	4.57	129.56
A2D	561	29.67	6.03	16.09	28.20	6.76	9.80	255.47
A2E	340	0.77	0.18	0.42	0.75	0.17	0.29	6.86
C11A	274	3.26	0.73	1.80	3.16	0.74	1.18	28.91
C11B	375	1.60	0.42	0.88	1.56	0.36	0.64	14.66
C11C	535	2.59	0.45	1.43	2.57	0.59	0.78	21.70
C11D	547	5.01	2.14	2.80	5.14	1.17	2.99	53.57
Total	4028	72.33	16.32	39.52	69.66	16.48	25.96	639.02

Table 4

Values characterizing EAQI_s for the analyzed regions

Region	$Q_{us-wint}$ [GJ/h]	W_{QUA} [GJ _p /GJ _{us}]	E_{sFE} [mg/(m ² ·h)]	W_{EEUA} [g/GJ _{us}]	W_{Qd} [W/m ²]	W_{Hav} [m/m]	Y_{WH}	EAQI _s [mg/m ² h]	Air quality
A2A	79.1	0.62	219.88	1105.8	63.2	1.09	10.86	2387.3	3
A2B	56.5	0.62	65.23	615.7	31.5	1.07	11.26	734.4	2
A2C	83.6	0.75	305.21	1469.0	69.7	1.20	8.93	2725.1	3
A2D	121.3	1.14	455.63	1999.7	82.3	1.09	10.86	4947.1	4
A2E	30.0	0.14	20.20	217.3	25.6	1.07	11.26	227.4	1
C11A	30.9	0.55	105.38	889.5	30.7	1.30	7.64	805.5	2
C11B	7.1	1.34	39.11	1970.4	7.2	1.50	5.37	210.2	1
C11C	71.9	0.25	40.58	286.1	36.7	1.07	11.26	456.9	2
C11D	38.2	1.22	98.02	1343.9	24.2	1.07	11.26	1103.4	2
Average	518.5 ^{a)}	0.73	158.65	1171.5	42.8	1.13	10.14	1608.8	3

^{a)}The value constitutes a sum

C11B – very good (large W_{Hav} value) and C11D – good, mainly thanks to detached building development and dispersion of emission sources. Values shown in Fig. 3 and Table 4 point to subareas A2D, A2C and A2A as to significant ($W_{Qd} > 65$ W/m²) urban heat island (UHI) generation sources, which can influence periodical circulation of air masses linked with pollution transfer.

4. CONCLUSIONS

The analyses of the EAQI values and additional criteria (W_{QUA} , W_{EEUA} , W_{Qd} coefficients) not only indicate the areas with deteriorated air quality but also identify the

reasons for this state, being the basis for the recovery program. The method for determination of EAQI, assumes isolating a city or its area from the whole energetic system. It gives a rationale for evaluation of the air quality inside a fixed balance protection, based on the analysis of an existing urban and energy structure. It also allows programming of the modernization activities of the structure aiming to improve air quality in the discussed area.

Energy air quality index is determined mostly for isolated areas within an agglomeration, with densely developed areas with stationary and mobile emission sources. It can also be calculated for other areas and as a mean value for a city. Determination of the EAQI factor may be vital for areas with existing continuous monitoring system of pollution concentrations, satisfying the conditions of measurement background. This may allow one to calculate relative $EAQI_{UA}/EAQI_{Bac}$ indexes and to determine correlations between used option of air quality index (AQI) and EAQI, suitable for a urban complex with specific geographical and climatic location.

LIST OF SYMBOLS

- EAQI – energy air quality index, $mg/(m^2 \cdot h)$
 $EAQI_s$ – energy air quality index for stationary emissions sources, $mg/(m^2 \cdot h)$
 $EAQI_t$ – energy air quality index for traffic exhaust emissions, $mg/(m^2 \cdot h)$
 E_{iUA} – emission rate of i -th pollution from the combustion sources in analyzed area UA, mg/s
 E_{EUA} – equivalent emission rate from combustion sources in area UA, mg/s
 E_s – mass emission rate of a pollutant, mg/s
 E_{sFi} – strength for a pollutant i emitted from low sources on the surface area F , mass low emission rate per unit area, $mg/(m^2 \cdot s)$ or $mg/(m^2 \cdot h)$
 E_{iFE} – strength for an equivalent pollutant emitted from traffic sources on the surface area F , $mg/(m^2 \cdot h)$ or $g/(m^2 \cdot year)$
 E_{sFE} – strength for an equivalent pollutant emitted from stationary (point) energy sources on the surface area F , $mg/(m^2 \cdot h)$ or $g/(m^2 \cdot year)$
 F_U – surface area UA, m^2
 H_B – building height, m
 h_s – geometric stack height (from the ground level), m
 k_{Ui} – emissive toxicity equivalent of i -th pollution in relation to SO_2
 Q_d – direct energy – total energy used in the building, J
 Q_{pUA} – primary energy of fuels combusted in low sources, in the analyzed surface, J
 Q_{us} – usable energy – total energy consumed by a building, J
 W_{Ei} – emission rate of i -th pollution per unit usable energy, g/GJ_{us}
 \bar{W}_{EEUA} – average area emission rate per unit usable energy (ecological costs coefficient for energy supply), g/GJ_{us}
 W_H – factor of technical conditions of emission, m/m
 W_C – street canyon factor, m/m
 W_{Qd} – urban area strength for direct energy consumption as the determinant for generating Urban Heat Island, W/m^2
 W_{QUA} – factor of energy costs for the energy supply structure, J/J

- Y_{WH} – coefficient taking into account technical conditions W_H of emission
 Y_{WC} – coefficient taking into account the street canyon factor W_C

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MOHAMED ALWAEI*

ECONOMIC CALCULUS OF THE EFFECTIVENESS OF WASTE UTILIZATION PROCESSED AS SUBSTITUTES OF PRIMARY MATERIALS

Along with technical and legal means, economic instruments are crucial components in the field of utilizing waste as substitutes of primary materials. Economic calculus of the effectiveness of replacing primary materials with secondary materials consists of determining the difference between the total costs of the production in which waste are used as secondary materials and the production in which primary materials are implemented. Choosing an appropriate method of calculation is significant when it comes to defining the effectiveness of substituting primary for secondary materials. The method should allow measuring and comparing the final results of investments. Also, it ought to be adjusted to the character of a given project. The aim of this paper is twofold. One is to review the area and to introduce the reader with methods of calculation of the effectiveness of waste utilization as secondary materials (literature review). Then the calculation of the effectiveness of the production in which certain wastes are utilized was proposed the effectiveness of waste utilization processed as substitutes of primary materials is analyzed. Looking at the calculation of economic effectiveness, one may assume that the production is profitable when the effectiveness index is higher for the production in which waste material is used.

1. INTRODUCTION

Waste management should always deal with the use of waste as substitutes for primary materials. Waste should also be utilized as a source of energy. Re-use of waste should be treated as a way of reducing environmental pollution.

The rules of market economy require meeting the regulations of economic calculus when it comes to undertake a business enterprise. Economic calculus allows evaluation of final results before initiating such an enterprise. It protects contractors against undertaking risky ventures and enables them to choose optimum solutions [1].

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While calculating the effectiveness of such enterprises, one needs to compare the input and output. Economic calculus of various projects can be presented either in a relative form or in an absolute one. The absolute form signifies the profitability of given ventures, and provides the possibility of comparing their effectiveness. The relative form defines the relationship between the amount of functional values that are utilized and work input destined for this purpose.

When examining the effectiveness of particular enterprises, one needs to take into account measuring instruments and consider the categories of input and output. In order to evaluate the investment in which secondary materials are implemented, a thorough analysis is needed. So far, there have been several varied methods of calculating economic effectiveness among which the drawn – calculi method is the most highly recommended. The method takes diverse solutions into consideration, and also presents the whole range of incurred costs. “Ecobalances” in which all costs (including disposal costs and the ones devoted to preserving good environmental conditions) are considered, present a specific case of economic calculi. Moreover, energy consumption is the most significant component in determining the profitability of a given enterprise [2].

Calculation of the actual level of the co-effectiveness is one of the most serious and, at the same time, one of the most difficult issues when investing in waste recycling [3]. Many researches on effectiveness of recycling were done by many authors. A notable exception is Duran’s *A model for assessing the economic viability of construction and demolition waste recycling* which in his case study develops a model to assess the economic viability of certain markets for recycled construction and demolition waste. Once the model is developed and the underlying assumptions outlined and analysed, the paper then proceeds to assess the impact of the imposition of environmental taxes and the use of subsidies on the economic construction and demolition waste recycling. The underlying methodology of the model developed is clear and has a wider international applicability and relevance to the study of construction and demolition waste recycling [4].

Battol presented economic potential of recycling business in Lahore, Pakistan. The paper presents the state of solid waste reuse and recycling in Lahore, Pakistan, discusses the problems, and proposes a recycling program and highlight the usefulness of such a program in solving the problems associated with municipal solid waste. Data on solid waste recycling were gathered from residents of low-, middle- and high-income groups, as well as from scavengers and junkshops. A cost analysis is presented to show the income that can be generated through a well planned recycling program. It is shown that 21.2% of all recyclable waste in Lahore is recycled, and it generates an amount of Rs. 271 million (US \$ 4.5 million) per year through the informal sector. However, if the recycling practice is owned by the formal sector, it can save an amount of Rs. 65 million by reducing the collection cost. If recycling is adopted as an

industry, it can generate revenues of Rs. 530 million (US \$ 8.8 million) per year and can also save enormous amount of energy, as well as the natural resources [5].

Hage analyzes the determinants of recycling efforts in Swedish households, and focuses on the case of packaging waste (i.e., paper, glass, plastic, and metal). The analysis builds on a theoretical framework that integrates norm-motivated behavior into a simple economic model of household choice by assuming that the individuals have preferences for maintaining a self-image as morally responsible, and thus norm compliant, persons. The study showed the importance of both economic and moral motivations and the interdependence between these, it is important that future policy efforts recognize this dual motivation rationale. One important implication of this finding is that policy should preferably be presented in “packages” emphasizing both the moral obligations of individual recycling efforts as well as the measures introduced to facilitate households’ efforts. For instance, if weight-based collection fees are implemented, supplementary information should stress the environmental importance of increased material recycling and thus not only direct attention towards the incentive effects of the policy instrument [6].

2. METHODS OF MEASURING THE CALCULUS OF THE EFFECTIVENESS LITERATURE REVIEW

Various methods of calculating of the effectiveness of waste utilized as secondary materials have been proposed. Among them there is one that aims at complex evaluation by analyzing the shaping of capital expenditure and the costs of production. It all comes down to calculating “absolute pay-back period” and “relative pay-back period”. Thanks to the input, especially input on technical advances, the annual economy of operating costs is observable. Consequently, the expenditure is reimbursed after some time [7]. The formulas are as follows:

- for absolute pay-back period

$$\frac{\delta_2}{\chi_1 - \chi_2} = T_a \quad (1)$$

- for “relative pay-back period”

$$\frac{\delta_2 - \delta_1}{\chi_1 - \chi_2} = \frac{\Delta_\delta}{O_\chi} \quad (2)$$

in which δ_1 , δ_2 – expenditure of technological progress, χ_1 , χ_2 – annual exploitation costs and O_χ – the exploitation costs savings.

Since the macro scale calculus signifies social effectiveness, the choice of the most rational solutions is probable. On the other hand, microscale calculus, based on in-

curred expenses and predicted effects, presents the situation after undertaking an investment project. Since the calculus cannot include the expenses that are not incurred by the project, one is not allowed to include the expenses connected with external infrastructure if a given enterprise does not have a share in financing the investment. However, fines for environmental pollution and all additional charges, including the ones destined for the whole infrastructure, need to be covered by the enterprise.

Simplified formula of the calculus of the complex effectiveness of investment has a form [8]:

$$E = \frac{(\Omega - \Psi) + \theta\mathcal{E}}{\Phi(\alpha + \vartheta) + \Gamma\alpha + \Phi\mathcal{E}(\alpha + \vartheta) + \Gamma\mathcal{E}\alpha}. \quad (3)$$

where Ω is the predicted annual production value, Ψ is the predicted annual current production cost (as proper cost decreased of amortization, credit's interest and increased of tax wages fund), $\theta\mathcal{E}$ is the additional effect nascent beyond the enterprise, Φ is the value of technological progress expenditure in the enterprise with cost of environment protection, α is the rate of discount level of projects financed by bank credit, defined in valid acts, ϑ is the averaged depreciation rate calculated according to valid trade regulations, $\Gamma\alpha$ are the expenditures for creating the stock of circulating assets, assumed as height of predicted assets after achievement of target productive ability, $\Phi\mathcal{E}$ is the value of investment expenditures beyond the enterprise, stimulated by given investment, $\Gamma\mathcal{E}\alpha$ are the additional expenditures beyond the enterprise for creating the stock of circulating assets connected with the plans stimulated by given investment. The condition of effectiveness is fulfilled when $E > 1$.

Extended formula of the calculus of the complex effectiveness of investment has a form

$$E = \frac{\sum_{t=0}^n \varphi_t (\Omega_t - \Psi_t) + \sum_{t=0}^n \varphi_t \theta\mathcal{E}_t}{\sum_{t=0}^n \varphi_t \theta_t + \sum_{t=0}^n \varphi_t \theta\mathcal{E}_t} \quad (4)$$

where t ($t = 0, 1, 2, 3, \dots, n$) are the sequence years of the computational period, φ_t is the discount coefficient, decreasing in following years (calculated for each year), θ_t is the capital expenditure for investment projects, $\theta\mathcal{E}$ is the additional capital expenditure beyond the enterprise (fundamental investment).

Secondary materials are said to be used as substitutes for primary materials. When it comes to market economy, the basic form of evaluation of secondary and raw materials should be calculated economically. The calculus of economic effectiveness consists in comparing total costs of the production in which secondary materials are used with the costs of production in which primary materials are utilized. Prices of secon-

dary materials are usually lower; nevertheless, processing costs and their consumption are higher because of additional technological treatments.

The effects of implementing waste utilized as secondary materials can be defined in terms of profit increase. It brought about reduction of production costs and the possible difference between the prices of products made from raw materials. The increase (or decrease) in the amount of total profit is calculated in the following way:

$$Y = \sum_{i=1}^n [(\xi\omega_i - \zeta\omega_i) - (\xi\zeta_i - \zeta\zeta_i)] \wp \omega_i, \quad (5)$$

where i is the consecutive number of a product, $\xi\omega_i$ is the real or planned average price of sold product, manufactured with waste as secondary materials, $\xi\zeta_i$ is the average price of sold product manufactured of raw materials, $\zeta\zeta_i$ is the elementary average production cost of product manufactured of raw materials, $\zeta\omega_i$ is the elementary average production cost of product manufactured with waste as raw materials, $\wp \omega_i$ – the quantity of production units of manufactured products with waste contribution as secondary materials.

The following condition needs to be fulfilled so that the production is profitable:

$$\xi\omega_i - \zeta\omega_i > \xi\zeta_i - \zeta\zeta_i$$

If a given enterprise bears the costs of waste storage while processing raw materials, these costs should be treated as the additional ones. Moreover, they have the influence on the final result of secondary waste utilization. If the application of secondary materials instead of primary ones does not change the value and price of the products, the increase (or decrease) in the amount of total profit Zn_1 is calculated in the following way:

$$\Delta Y_1 = \sum_{i=1}^n (\zeta\zeta_i - \zeta\omega_i) \wp \omega_i \quad (6)$$

3. EVALUATION OF THE EFFECTIVENESS OF WASTE UTILIZED AS SUBSTITUTES FOR PRIMARY MATERIALS

Economic effectiveness is a result of economic activity. It is defined as a ratio of final effects in the period of economic operation to incurred costs. The basic problem of every enterprise is estimation of its effectiveness. The instrument on the basis of which the management process is evaluated is the economic calculus. Economic calculus is a foundation for the decision of whether to undertake the enterprise or not. It consists of comparing the input and output while taking into account various divisions of the factors of production [9].

The choice of waste calculation is of great importance when it comes to determining the effectiveness of waste utilized as substitutes for primary materials. The applied method should allow measuring and comparing the effects of various enterprises and activities; nevertheless, it ought to be adjusted to the character of such an enterprise.

Production of waste used as substitutes for primary materials involves undertaking various activities. As a result, determining the economic effectiveness of the production does not always allow defining the production entirely. It often happens that particular stages of the production, such as recovery of secondary materials, their treatment, and processing should also be determined. The calculus of the effectiveness of the production in which certain wastes are utilized can be calculated as follows:

$$v = \rho - v \quad (7)$$

where

$$\rho = \sum_i^n \xi \omega_i \wp \omega_i, \quad v = \sum_i^n \zeta \omega_i \wp \omega_i, \quad \rho > v$$

in which v is the difference between value of sale and total cost of operation, ρ is the value of sale of batch with waste as secondary materials, v is the total cost of batch after analyzed operations.

The costs of waste processing used as substitutes for secondary materials are different from the once processed as substitutes for primary materials. It often happens that the costs of secondary materials are lower, but the costs of waste processing are higher because of additional and purifying treatments or else due to lower capacity. Consequently, the calculus of economic effectiveness comes down to determining the difference between the total costs of the production in which wastes are used as primary materials and the costs of methods in which primary materials are used [10].

In order to calculate economic effectiveness E of productions that do not include capital expenditure, we need to make calculations and compare the effectiveness of relative production in which wastes are used. The wastes are utilized as substitutes for secondary materials and primary materials, respectively. To make calculations of profitability index, we implement the following dependence:

$$E = \frac{\sum_i^n (\xi \omega_i - \zeta \omega_i) \wp \omega_i}{\sum_i^n \zeta \omega_i \wp \omega_i} \quad (8)$$

To examine the profitability of the production with waste used as substitutes for primary materials, we need to calculate separately the effectiveness index obtained from the production of primary materials (E_{ζ}) and the profitability index gained from the production of secondary materials (E_{ω}).

Based on Equation (8), the effectiveness index of the production of primary materials is as follows:

$$E_{\zeta} = \frac{\sum_i^n (\xi_{\zeta_i} - \zeta_{\zeta_i}) \wp \omega_i}{\sum_i^n \zeta_{\zeta_i} \wp \omega_i} \quad (8a)$$

while the effectiveness index of the production of secondary materials is:

$$E_{\omega} = \frac{\sum_i^n (\xi_{\omega_i} - \zeta_{\omega_i}) p_{w_i}}{\sum_i^n \zeta_{\omega_i} \wp \omega_i} \quad (8b)$$

Consequently, the production is profitable if:

$$E_{\omega} \geq E_{\zeta}$$

4. DISCUSSION

Traditional analysis of costs and merits should be enriched by including various costs to the economic calculus. These costs are connected with the resources taken directly or indirectly from the natural environment. Through implementing appropriate methods, qualitative features of environment that are difficult to measure can be considered in terms of money [11].

Along with technical, legal, and organizational treatments, economic instruments play a significant role in the field of environmental protection since dealing with environmental risk is examined on the economic level. As a result, environmental protection is said to be an important economic activity.

The choice of appropriate measuring instruments is important when it comes to examining the effectiveness of economic enterprises. To examine the profitability of the production with waste used as substitutes for primary materials, we needed to separately calculate the effectiveness index obtained from the production of primary materials and the profitability index gained from the production of secondary materials. Looking at the calculation of economic effectiveness, one may assume that the production is profitable when the effectiveness index is higher for the production in which waste material is used.

Altogether more than 1.7 billion tons of wastes are landfilled in Poland (state on end of 2007 year) and every year this amount increases approximately by 133 million

tons. Unfortunately, according to the statistics for the whole Poland, landfill is the main disposal method. The data show that waste deposited varies between 96% and 98%. Other methods are used on a negligible scale. Due to requirements of recycling and in order to achieve the levels of recycling and decrease amount of waste directed to landfills defined in EU directives and Polish acts, presented method included in Sect. 3, where the effectiveness of waste utilization processed as substitutes of primary materials were analyzed, might be a good way for optimization the cost-effectiveness of existent plant and planning new plants of waste utilization as substitute raw materials.

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BOLESŁAW TABIŚ*, ROBERT GRZYWACZ*

ASSESSMENT OF FINITE DIMENSIONAL APPROXIMATIONS IN INTEGRATION OF SPHERICAL BIOFILMS FOR MICROBIOLOGICAL PROCESSES

In various biotechnological processes such as biodegradation of toxic organic compounds, microorganisms are immobilized on inert carriers. Three-phase fluidized-bed bioreactors and airlift apparatus are examples of devices in which microorganisms are immobilized as a thin layer of biomass on fine pellets. Due to a spherical shape of the carrier, the resultant layer of microorganisms has also spherical geometry. In the paper, a quantitative assessment has been made of numerical methods for determining the distributions of reagent concentrations and the effectiveness factors of a biofilm in the form of spherical layers. Calculations have been done for aerobic biodegradation of phenol.

1. INTRODUCTION

Research into the growing mechanism and the properties of a biofilm, i.e. a layer of microorganisms on solid media, has been conducted for approximately thirty years [1, 2], though the phenomenon itself was discovered earlier [3, 4]. Water and sanitary engineering specialists have largely contributed to the advancement of this research. Literature concerning related problems seems to be abundant. Major applications of biofilm engineering, however, are associated with developments in biotechnology when new types of bioreactors were constructed. Monitored biofilm growth with controllable biocenosis is used in such devices as: biofilters, membrane bioreactors and three-phase fluidized-bed and airlift bioreactors with the biofilm grown on fine inert pellets. The paper deals with three methods for numerical simulation of the microbiological processes occurring in biofilms grown on spherical carriers which are often used in three-phase fluidized-bed bioreactors.

Three-phase fluidized-bed bioreactors have been used for multiple implementations. They are employed, among others, in the processes of microbiological degrada-

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tion [5–8]. The advantages of such bioreactors include, above all, highly developed interphase surface, simple design, and first and foremost the separation of the residence time of liquid from that of biomass in the reactors. This enables the hold-up of biomass in the bioreactor for sufficiently high liquid flow rates.

A quantitative description of a microbiological process in a three-phase bioreactor consists of mass balances for the liquid and solid phases. The solid phase is the biofilm grown on an inert carrier. Of particular importance are the balances of the microbiological process in the biofilm, as the latter constitutes an environment in which biochemical processes can take place. The balances are derived in the form of differential equations which describe the distributions of concentrations of species within the biofilm. The effectiveness factor of the biofilm and the average rates of the process within it are determined in this way.

The existing literature, even so famous work as IWA report on biofilm modelling [3], provides no data to assess and compare the efficiency of any quick and relatively simple methods for the integration of biofilms and the calculation of their effectiveness factors. Therefore the so-called finite dimensional approximation which can be used for the calculation of the microbiological processes occurring in biofilms, are discussed and assessed. The methods of orthogonal collocation and finite differences are examined and compared with the shooting method, which is accepted as a reference. The interested reader could easily modify any part of the algorithms in question, and create their own numerical procedures.

The calculations were performed for the aerobic biodegradation of phenol using *Pseudomonas putida* bacteria. The experimentally determined kinetic equations by Seker et al. have been used to describe the uptake rate of the carbonaceous substrate and oxygen [9].

2. MICROBIOLOGICAL PROCESS IN A SPHERICAL BIOFILM AND ITS MATHEMATICAL MODEL

It was shown [10] that an aerobic microbiological process occurring in the biofilm grown on an inert spherical pellet can be described using a system of two non-linear differential equations:

$$\frac{d^2\beta}{dz^2} + \frac{2\delta}{r_0 + \delta z} \frac{d\beta}{dz} - \Phi_A^2 \frac{r_A(\beta, \gamma)}{r_{As}} = 0 \quad (1a)$$

$$\frac{d^2\gamma}{dz^2} + \frac{2\delta}{r_0 + \delta z} \frac{d\gamma}{dz} - \Phi_1^2 \frac{r_T(\beta, \gamma)}{r_{Ts}} = 0 \quad (1b)$$

with the boundary conditions:

$$\frac{d\beta(0)}{dz} = \frac{d\gamma(0)}{dz} = 0 \quad (2a)$$

$$\beta(1) = \gamma(1) = 1 \quad (2b)$$

where

$$\beta = \frac{c_A^b}{c_{As}}, \quad \gamma = \frac{c_T^b}{c_{Ts}}, \quad \Phi_A^2 = \frac{\delta^2 r_{As}}{D_{Ae} c_{As}}, \quad \Phi_T^2 = \frac{\delta^2 r_{Ts}}{D_{Te} c_{Ts}}$$

whereas the dimensionless coordinate in the biofilm has been defined as

$$z = \frac{x - r_0}{\delta} \in [0, 1]$$

with x serving as the current coordinate. Reference rates r_{As} and r_{Ts} are calculated for concentrations at the biofilm surface.

Uptake rates of carbonaceous substrate and oxygen are determined according to Seker et al. [9] as follows:

$$r_A(\beta, \gamma) = \frac{1}{w_{BA}} f_1(c_A(\beta)) f_2(c_T(\gamma)) \rho_b$$

$$r_T(\beta, \gamma) = \frac{1}{w_{BT}} f_1(c_A(\beta)) f_2(c_T(\gamma)) \rho_b$$

where

$$f_1(c_A) = \frac{kc_A}{K_s + c_A + \frac{c_A^2}{K_{in}}}, \quad f_2(c_T) = \frac{c_T}{K_T + c_T}$$

The method of orthogonal collocation can be characterized more easily by using the example of a single differential equation. Let us assume then that the following boundary value problem (BVP) should be solved:

$$\frac{d^2 y}{dz^2} + \frac{2\delta}{r_0 + \delta z} \frac{dy}{dz} - \Phi^2 \frac{r_A(y)}{r_{As}} = 0 \quad (3)$$

$$\frac{dy(0)}{dz} = 0 \quad (4a)$$

$$y(1) = 1, \quad z \in [0, 1] \quad (4b)$$

The use of finite dimensional approximation in the form of orthogonal collocation to solve the boundary value problem consists in approximating a function $y(z)$ being the solution of BVP by a polynomial of a certain degree [11]. It is assumed that the polynomials have the following form:

$$y = \sum_{i=1}^{N+1} a_i z^{2i-2} = f(z^2) \quad (5)$$

Polynomials $f(z^2)$ are constructed subject to an orthogonality constraint, i.e. any two of polynomials $f_{m-1}(z^2)$ and $f_m(z^2)$ are required to fulfill the condition:

$$\int_0^1 f_{m-1}(z^2) f_m(z^2) dz = 0 \quad (6)$$

Given that $f_0(z^2) = a_0 = 1$, then Eq. (6) provides the basis for determining further polynomials. By doing so, formulas have been derived for the first four polynomials which are used throughout this paper:

$$f_1(z^2) = 1 - 3z^2 \quad (7a)$$

$$f_2(z^2) = 1 - 10z^2 + \frac{35}{3}z^4 \quad (7b)$$

$$f_3(z^2) = 1 - 21z^2 + 63z^4 - \frac{231}{5}z^6 \quad (7c)$$

$$f_4(z^2) = 1 - 36z^2 + 198z^4 - \frac{1716}{5}z^6 + \frac{184\,041}{1001}z^8 \quad (7d)$$

Table 1 shows the positive roots of these polynomials. These roots are referred to as internal collocation points. A solution to equation (3) is sought at these points.

Table 1

Positive roots of the polynomials (7)
(internal collocation points)

Polynomial	Collocation points
$f_1(z^2)$	0.5773502692
$f_2(z^2)$	0.3399810436 0.8611363116
$f_3(z^2)$	0.2386191861 0.6612093865 0.9324695142
$f_4(z^2)$	0.1834346425 0.5255324099 0.7966664774 0.9602898565

Let $j = 1, 2, \dots, N$ be a set of internal collocation points, i.e. the points lying within the interval $z \in [0, 1]$. Then the value of function (5) at the j th collocation point is equal to $y_j = y(z_j)$. The solutions for all collocation points can then be written using vector notation as follows:

$$\mathbf{y} = \mathbf{Q} \cdot \mathbf{a} \quad (8)$$

where the elements of matrix \mathbf{Q} are calculated as $q_{ji} = z_j^{2i-2}$.

The derivative dy/dz at the collocation point z_j is calculated from the dependence:

$$\frac{dy_j}{dz} = \sum_{i=1}^{N+1} \frac{d}{dz} (a_i z_j^{2i-2}) \quad (9)$$

A single relation can be employed as above to express the derivatives for all collocation points using vector notation:

$$\frac{d\mathbf{y}}{dz} = \mathbf{C} \cdot \mathbf{a} \quad \text{where} \quad c_{ji} = \frac{d}{dz} z_j^{2i-2} \quad (10)$$

Since $\mathbf{y} = \mathbf{Q} \cdot \mathbf{a}$, then $\mathbf{Q}^{-1} \cdot \mathbf{y} = \mathbf{a}$, thus Eq. (10) can be expressed as follows:

$$\frac{d\mathbf{y}}{dz} = \mathbf{C} \cdot \mathbf{Q}^{-1} \cdot \mathbf{y} = \mathbf{B} \cdot \mathbf{y} \quad (11)$$

Second derivative d^2y/dz^2 at the point z_j , in turn, is defined by the equation:

$$\frac{d^2y_j}{dz^2} = \sum_{i=1}^{N+1} \frac{d^2}{dz^2} (a_i z_j^{2i-2}) \quad (12)$$

For all collocation points, we have then:

$$\frac{d^2\mathbf{y}}{dz^2} = \mathbf{D} \cdot \mathbf{a} = \mathbf{D} \cdot \mathbf{Q}^{-1} \cdot \mathbf{y} = \mathbf{G} \cdot \mathbf{y} \quad (13)$$

After substituting the expressions with derivatives of the first and second order into Eq. (3), a system of $N+1$ non-linear algebraic equations is obtained with respect to y_1, y_2, \dots, y_{N+1} variables, while $y_{N+1} = y(z_{N+1}) = y(1)$

$$\sum_{i=1}^{N+1} g_{ji} y_i + \frac{2\delta}{r_0 + \delta z_j} \sum_{i=1}^{N+1} b_{ji} y_i - \frac{\Phi^2}{r_{As}} r_A(y_j) = 0, \quad j = 1, 2, \dots, N \quad (14a)$$

$$y_{N+1} - 1 = 0 \quad (14b)$$

Coefficients g_{ji} and b_{ji} are the components of predefined matrices \mathbf{G} and \mathbf{B} .

The use of the collocation method to determine the concentrations of the carbonaceous substrate and oxygen in the biofilm (Eqs. (1a), (1b)) consists in solving the system of $2(N+1)$ non-linear algebraic equations:

$$\sum_{i=1}^{N+1} g_{ji} \beta_i + \frac{2\delta}{r_o + \delta z_j} \sum_{i=1}^{N+1} b_{ji} \beta_i - \frac{\Phi_A^2}{r_{As}} r_A(\beta_j, \gamma_j) = 0, \quad j = 1, 2, \dots, N \quad (15a)$$

$$\beta_{N+1} - 1 = 0 \quad (15b)$$

$$\sum_{i=1}^{N+1} g_{ji} \gamma_i + \frac{2\delta}{r_o + \delta z_j} \sum_{i=1}^{N+1} b_{ji} \gamma_i - \frac{\Phi_T^2}{r_{Ts}} r_T(\beta_j, \gamma_j) = 0, \quad j = 1, 2, \dots, N \quad (15c)$$

$$\gamma_{N+1} - 1 = 0 \quad (15d)$$

Another finite dimensional approximation is the grid method, or in other words, the method of finite differences. In this approach, a set of points is generated in equal distances h within the integration interval $z \in [0, 1]$. These points make up the nodes of the grid. Equations for the approximation of derivatives are inscribed in the grid nodes and boundary conditions, using appropriate finite differences. If M nodes are placed across an integration interval, the determination of concentration distributions in the biofilm, i.e. the solution of differential problem (1)–(2), is reduced to solving the following system of $2M$ nonlinear algebraic equations:

$$-3\beta_1 + 4\beta_2 - \beta_3 = 0, \quad i = 1 \quad (16a)$$

$$\frac{\beta_{i+1} - 2\beta_i + \beta_{i-1}}{h^2} + \frac{2\delta}{r_o + \delta z_i} \frac{\beta_{i+1} - \beta_{i-1}}{2h} - \frac{\Phi_A^2}{r_{As}} r_A(\beta_i, \gamma_i) = 0, \quad i = 2, 3, \dots, M-1 \quad (16b)$$

$$\beta_M - 1 = 0 \quad (16c)$$

$$-3\gamma_1 + 4\gamma_2 - \gamma_3 = 0, \quad i = 1 \quad (16d)$$

$$\frac{\gamma_{i+1} - 2\gamma_i + \gamma_{i-1}}{h^2} + \frac{2\delta}{r_o + \delta z_i} \frac{\gamma_{i+1} - \gamma_{i-1}}{2h} - \frac{\Phi_T^2}{r_{Ts}} r_T(\beta_i, \gamma_i) = 0, \quad i = 2, 3, \dots, M-1 \quad (16e)$$

$$\gamma_M - 1 = 0$$

where $i = 1, 2, \dots, M$ refers to i th grid node.

The efficiency of both finite dimensional approximation methods has been compared with that of the shooting method. Its algorithm has previously been tested for linear kinetics, for which an analytical solution is available. By comparing the analytical results with those obtained using the shooting method it has been confirmed that the latter is sufficiently accurate in the sense that the results with repeatability of even eight significant digits are fully achievable. The tests have demonstrated that the rela-

tive error of the shooting method compared to the analytical solution does not exceed $5 \cdot 10^{-5}\%$.

To solve the boundary value problem (1)–(2) using the shooting method, let us introduce the following denotations:

$$y_1 = \beta, \quad y_2 = \frac{dy_1}{dz} = \frac{d\beta}{dz}, \quad \frac{dy_2}{dz} = \frac{d^2\beta}{dz^2}$$

$$y_3 = \gamma, \quad y_4 = \frac{dy_3}{dz} = \frac{d\gamma}{dz}, \quad \frac{dy_4}{dz} = \frac{d^2\gamma}{dz^2}$$

Then the system of Eqs. (1) with conditions (2) can be presented as follows:

$$\frac{dy_1}{dz} = y_2 \quad (17a)$$

$$\frac{dy_2}{dz} = -\frac{2\delta}{r_o + \delta z} y_2 + \Phi_A^2 \frac{r_A(y_1, y_3)}{r_{As}} \quad (17b)$$

$$\frac{dy_3}{dz} = y_4 \quad (17c)$$

$$\frac{dy_4}{dz} = -\frac{2\delta}{r_o + \delta z} y_4 + \Phi_T^2 \frac{r_T(y_1, y_3)}{r_{Ts}} \quad (17d)$$

$$y_2(0) = y_4(0) = 0 \quad (18a)$$

$$y_1(1) = y_3(1) = 1 \quad (18b)$$

To integrate the system of Eqs. (17) within the interval from $z = 0$ to $z = 1$, missing boundary conditions $y_1(0) = x_1$ and $y_3(0) = x_2$ should be assumed, and then it should be verified whether the conditions for $z=1$ are fulfilled, i.e. whether $y_1(1) = 1$ and $y_3(1) = 1$. Such reasoning reduces the solution of the boundary value problem to solving the system of non-linear equations:

$$f_1(\mathbf{x}) = y_1(1) - 1 \quad (19a)$$

$$f_2(\mathbf{x}) = y_3(1) - 1, \quad \mathbf{x} = (x_1, x_2) \quad (19b)$$

As described here, the shooting method consists of an algorithm to integrate system of differential equations (17) with an imposed superordinated algorithm to solve the system of algebraic solutions (19). The fourth order Runge–Kutta method with the integration step $\Delta z = 0.005$ has been used to integrate Eqs. (17), whereas system of Eqs. (19) has been solved using the Newton method, including numerical calculation of the Jacobi matrix.

3. DISCUSSION OF THE RESULTS

The sought solution to differential equations (1) with boundary conditions (2) are the functions describing the dimensionless concentration of carbonaceous substrate $\beta(z)$ and dimensionless concentration of oxygen $\gamma(z)$ over the biofilm. These functions, also called concentration profiles, indicate possible depletion of particular species inside the biofilm. Its thickness can be controlled on this basis, e.g. to protect microorganisms from anoxia.

The efficiency of the orthogonal collocation method with the shooting one, which is accepted as a reference, is compared in Table 2. A minimum number of internal collocation points N have been selected to determine the application limits of the collocation method. For better clarity, only the function $\beta(z)$ describing the dimensionless carbonaceous substrate concentration has been presented.

Table 2

Distribution of dimensional concentration of carbonaceous substrate in biofilm $\beta(z)$ obtained for $\Phi_A = 3$ by the shooting method and by orthogonal collocation and relative error of orthogonal collocation Δ

z	Shooting method	Orthogonal collocation			
		$N = 2$	Δ [%]	$N = 4$	Δ [%]
0.0	0.0902930	0.1007690	11.6	0.0929365	2.93
0.2	0.1130351	0.1192938	5.54	0.1140572	0.90
0.4	0.1834807	0.1836903	0.11	0.1835787	0.052
0.6	0.3225195	0.3198253	-0.83	0.3226893	0.053
0.8	0.5732899	0.5716100	-0.29	0.5733580	0.012
1.0	1.0000000	1.0000000	0.00	1.0000000	0.00

As appears from Table 2, the selection of only two internal collocation points is sufficient to produce qualitative, and even quantitative estimates as the approximation error does not exceed 1% for coordinate $z \geq 0.4$. Extending the number of the collocation points up to four brings already satisfactory results.

A similar quantitative comparison is provided in Table 3, which shows functions $\beta(z)$ obtained using the method of finite differences. As in the previous case, it has been compared with the shooting method. Two values of the grid nodes have been assumed for calculations, namely: $M = 10$ and $M = 20$. In this case however, the effect of doubling the number of nodes is less effective than in the collocation method. If the number of nodes is increased from $M = 10$ to $M = 20$ in the finite difference method, the approximation error decreases by 3.8% on average, whereas changing $N = 2$ to $N = 4$ in the collocation method reduces such error by tenfold.

Table 3

Distribution of dimensional concentration of carbonaceous substrate in biofilm $\beta(z)$ obtained for $\Phi_A = 3$ by the shooting method and by the finite differences algorithm and relative error of the finite differences method Δ

z	Shooting method	Method of finite differences			
		$M = 10$	Δ [%]	$M = 20$	Δ [%]
0.0	0.0902930	0.09225949	2.18	0.0909143	0.69
0.2	0.1130351	0.1146772	1.45	0.1134991	0.41
0.4	0.1834807	0.1850648	0.86	0.1838998	0.23
0.6	0.3225195	0.3239721	0.45	0.3228925	0.12
0.8	0.5732899	0.5742480	0.17	0.5735327	0.04
1.0	1.0000000	1.0000000	0.00	1.0000000	0.00

As results from Tables 2 and 3, the approximation is the least accurate at the support of the biofilm, i.e. for $z = 0$. The nearer the surface of the biofilm, the more accurate the approximation of concentration distribution becomes. Therefore, apart from comparing the profiles themselves, a measure relating to the biofilm as a whole has to be introduced to assess the approximations used. Such a measure is the effectiveness factor of the biofilm which is calculated from:

$$\eta = \frac{r_{Aav}}{r_{As}} \quad (20)$$

where

$$r_{Aav} = \frac{3\delta}{(r_o + \delta)^3 - r_o^3} \int_0^1 (r_o + \delta z)^2 r_A [\beta(z), \gamma(z)] dz \quad (21)$$

As can be seen from the form of Eq. (21) representing the average rate of the bio-process, it contains information on the entire concentration profiles of both reagents, and therefore it can be used as a reliable measure of accuracy when determining functions $\beta(z)$ and $\gamma(z)$. The effectiveness factors of the biofilm calculated using the shooting and the orthogonal collocation methods are compared in Table 4. A similar comparison to the method of finite differences is given in Table 5. For better clarity, graphical comparison of the results discussed is presented in Fig. 1, where relative error Δ is computed as

$$\Delta = \frac{\eta_{\text{approx.}} - \eta_{\text{shooting}}}{\eta_{\text{shooting}}} \cdot 100\% \quad (22)$$

where $\eta_{\text{approx.}}$ denotes η obtained by any finite dimensional approximation algorithm whereas η_{shooting} means the η calculated by shooting method.

Two conclusions can be drawn from the data presented in Tables 4 and 5 as well from Fig. 1, both of them cognitive and practical in nature:

- The orthogonal collocation method can be used for processes characterized by even large values of the Thiele modulus.
- Doubling the number of nodes when calculating the effectiveness factor of the biofilm is much more effective in the collocation method than in the finite difference method.

Table 4

Effectiveness factors of a biofilm η obtained by the shooting method and by the orthogonal collocation
(Δ means the relative error of the orthogonal collocation)

Φ_A	Shooting method	Orthogonal collocation			
		$N = 2$	Δ [%]	$N = 4$	Δ [%]
0.1	0.99895	0.99897	0.002	0.99896	0.001
0.2	0.99580	0.99588	0.008	0.99583	0.003
0.5	0.97397	0.97445	0.049	0.97414	0.017
1.0	0.89990	0.90162	0.19	0.90048	0.064
2.0	0.68538	0.68874	0.49	0.68602	0.093
3.0	0.51409	0.51476	0.13	0.51451	0.082
5.0	0.33319	0.30869	-7.3	0.33324	0.015
7.0	0.24539	0.18003	-26.6	0.24542	0.012
10.0	0.17565	0.06095	-65.3	0.17572	0.039

Table 5

Effectiveness factors of a biofilm η obtained by the shooting method and by the finite differences algorithm
(Δ means the relative error of the finite differences method)

Φ_A	Shooting method	Method of finite differences			
		$M = 10$	Δ [%]	$M = 20$	Δ [%]
0.1	0.99895	0.99897	0.002	0.99896	0.001
0.2	0.99580	0.99582	0.002	0.99581	0.001
0.5	0.97397	0.97408	0.011	0.97400	0.003
1.0	0.89990	0.90031	0.045	0.90001	0.012
2.0	0.68538	0.68636	0.14	0.68565	0.039
3.0	0.51409	0.51546	0.27	0.51446	0.072
5.0	0.33319	0.33571	0.76	0.33384	0.15
7.0	0.24539	0.24910	1.5	0.24636	0.39
10.0	0.17565	0.18096	3.0	0.17709	0.82

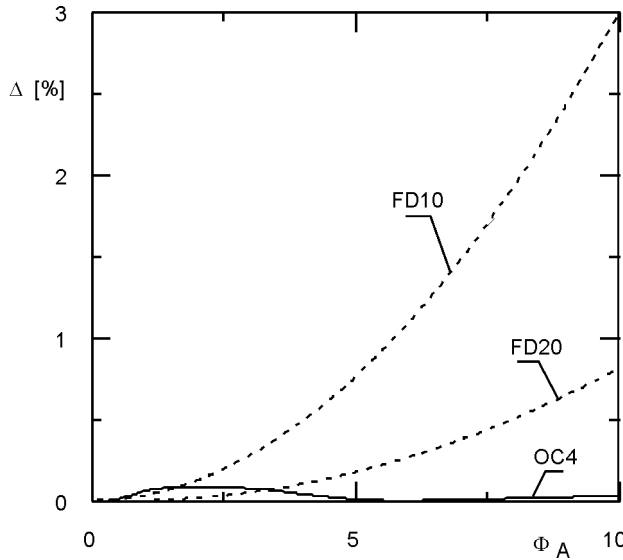


Fig. 1. Relative errors Δ in computing of the effectiveness factor of a biofilm by the orthogonal collocation with four collocation points (OC4) and by the finite difference algorithm with 10 (FD10) and 20 nodes (FD20)

4. CONCLUSIONS

Two finite dimensional approximation methods for integration of models describing biofilms with spherical geometry have been presented. They can be used for the modelling, design, and operational simulations of bioreactors with an immobilized biofilms of microorganisms, both on mobile carriers, such as in fluidized bed or airlift bioreactors, and on fixed carriers that are found in three-phase aerobic bioreactors with packed beds.

Table 6

Relative time of computation required for approximate methods in comparison with the shooting method

Shooting method	Method of orthogonal collocation		Method of finite differences	
	$N = 2$	$N = 4$	$M = 10$	$M = 20$
$\Delta z = 0.005$				
1	0.122	0.496	0.288	1.255

The efficiency of the approaches under investigation has been assessed quantitatively, both in terms of the accuracy of calculations and the time required for such calculations. Table 6 contains a specification of the relative computation times required in the finite dimensional approximations as compared to the shooting method.

These are the means obtained from the calculations for various values of the Thiele modulus. For instance, the collocation method with $N=4$ internal points requires 0.496 of the time that is needed for the shooting method. The data in Table 6 also indicates that the method of finite differences with the number of nodes $M=20$ is 1.255 times slower than the shooting method.

It has been demonstrated that the orthogonal collocation method is advisable for not very large values of the Thiele modulus. Then a sufficiently accurate solution can be obtained within the shortest time. A larger number of collocation points should be used, however, when the values of the Thiele modulus are higher.

All the numerical methods discussed can also be used for the integration of any other objects with spherical symmetry, e.g. fully active biocatalyst pellets. It is then sufficient to assume $r_0 = 0$ in the equations presented above.

SYMBOLS

c_A, c_T	– concentration of carbonaceous substrate A and oxygen T, respectively, $\text{kg}\cdot\text{m}^{-3}$
D_e	– effective diffusion coefficient of the biofilm, $\text{m}^2\cdot\text{h}^{-1}$
h	– distance between grid nodes
M	– number of nodes in the finite difference method
N	– number of internal collocation points
r_A, r_T	– consumption rate of carbonaceous substrate A and oxygen T, $\text{kg}\cdot\text{m}^{-3}\cdot\text{h}^{-1}$
r_0	– radius of the inert carrier, m
w_{BA}, w_{BT}	– yield coefficients
z	– dimensionless coordinate in the biofilm
β	– dimensionless concentration of carbonaceous substrate
γ	– dimensionless concentration of oxygen
δ	– biofilm thickness, m
η	– effectiveness factor of the biofilm
ρ_b	– biofilm density, $\text{kg B}\cdot\text{m}^{-3}$
Δ	– relative error of finite dimensional approximation tested, %
Φ	– Thiele modulus

SUBSCRIPTS AND SUPERSCRIPTS

A	– limiting carbonaceous substrate
B	– biomass
T	– oxygen
s	– external surface of the biofilm
b	– biofilm

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PHYSIOLOGICAL AND BIOCHEMICAL ACTIVITY OF SPRING WHEAT (*TRITICUM VULGARE*) UNDER THE CONDITIONS OF STRESS CAUSED BY CADMIUM

The effect of cadmium on physiological and biochemical activity of spring wheat cv. Alba was studied within the concentrations of 0.025–5 mM. The content of chlorophyll a and b, carotenoids, the intensity of assimilation of CO₂ and transpiration as well as the activity of catalase, peroxydase, superoxide dismutase in the phase of two cotyledones and in the phase of shooting in wheat were determined. The applied doses of cadmium significantly decreased the content of determined assimilation dyes, reduced the intensity of assimilation of CO₂ and transpiration and caused an increase in the index of use of water in the photosynthesis in all the studied growth phases of spring wheat. A clear stimulating influence of the applied doses of cadmium on the activity of catalase, peroksydase and superoxide dismutase in spring wheat was noticed.

1. INTRODUCTION

As compared to other metals [1], cadmium is characterised by the largest concentration both in the soil and in the plant. Due to its high mobility, bioavailability and characteristic physicochemical properties it was regarded the metal of particularly high toxicity [2, 3]. Its presence causes blockades of key metabolic reactions by destabilization of functional groups and by structural changes of the enzymes engaged in the reactions [4–7]. One of the most dangerous effects of the activity of cadmium, due to its non-specific and reactive character, is generating reactive form of oxygen, including free radicals leading to considerable damages in the lipid composition of membranes [3, 8–10]. Typical reactions of neutralization of the excessive reactive forms of oxygen can be the activation of antioxidative enzymes, i.e. catalase, peroxidase and superoxide dismutase [11–13].

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The aim of the study was to determine the activity of oxidative stress enzymes (catalase, peroxidase and superoxide dismutase), the content of assimilation dyes and the intensity of CO₂ assimilation and transpiration in various growth stages of wheat growing in soil with the addition of cadmium and fertilized with NPK (nitrogen, phosphorous, and potash).

2. MATERIALS AND METHODS

Spring wheat cv. Alba was taken for the investigation. Two series of experiments were carried out in three replications in controlled conditions at 23 °C, light intensity 100 $\mu\text{E}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$, photoperiodism 12/12 h. The soil used in the experiment belonged to the good wheat complex 2 soil of light silty loam composition and the 1.2% content of organic carbon. Humidity of the soil was kept at the level of 60% of maximum water capacity. Cadmium was introduced to the soil in the form of water solutions of cadmium nitrate ($\text{Cd}(\text{NO}_3)_2$), in the following concentrations: 0.025, 0.05, 0.5 and 5 mM, whereas fertilizers in the form of water solutions, according to the recommendations for the good wheat complex 2 soil – 115 kg N·ha⁻¹, 50 kg P₂O₅·ha⁻¹, 30 kg K₂O·ha⁻¹. The following combinations were used in the experiment: 1 – the control, 2 – NPK, and samples containing NPK with cadmium in the following doses: 3 – NPK + 0.025 mM; 4 – NPK + 0.05 mM; NPK + 0.5 mM; 6 – NPK + 5 mM, 7 – 0.025 mM; 8 – 0.05 mM; 9 – 0.5 mM; 10 – 5 mM. The differentiated doses of cadmium and fertilizers were added to the soil according to the experimental combination. Germinated grains of wheat were sown to the soil prepared in this way. The determination of the studied parameters (the content of chlorophyll a and b, carotenoids, the intensity of CO₂ assimilation and transpiration, and the activity of catalase, peroxidase and superoxide dismutase) were carried out in two growth phases of the plant: two cotyledons (the 7th day of the studies) and shooting (14th, 21st, 28th day of the studies). The content of assimilation pigments in leaves was determined by means of the Lichtenthaler and Welburn method [14]. The intensity of photosynthesis and transpiration was measured (repeating the measurement four times) using the TPS-2 gas analyzer manufactured by PP Systems (UK), at constant lighting 2053 $\mu\text{mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$. Based on the obtained results of the intensity of assimilation and transpiration photosynthetic effectiveness of the use of water (ω_F) was calculated. The activity of peroxidase was defined by the Chance and Machly method [15], the activity of catalase by Lück's method [16] and that of superoxide dismutase, using the method of Abassi et al. [17].

The results were worked out by means of the method of two-factor variance using the Duncan test at a significance level $\text{NIR}_{0.05}$. Using the Pearson's linear correlation coefficient (r), correlation between the concentration of cadmium in leaves and the examined physiological features of wheat was shown.

3. RESULTS AND DISCUSSION

Spring wheat cv. alba was characterised by a differentiated content of photosynthetic pigments, the activity of catalase, peroxidase and superoxide dismutase and the intensity of CO₂ assimilation and transpiration depending on the level of soil contamination with cadmium (Tables 1–3, Fig. 1).

A significant influence of cadmium was observed on the content of photosynthetic pigments and the intensity of CO₂ assimilation and transpiration of spring wheat. A negative effect of interaction time of cadmium on the defined physiological parameters was also noticed. Mineral fertilization increased the amount of chlorophyll a and b and of carotenoids, and it slightly changed the intensity of CO₂ assimilation and transpiration in the examined plant. Under fertilization, the average content of chlorophyll a increased by 6%, chlorophyll b by 14%, and carotenoids by 13% as compared to the control plants (Table 1).

The applied doses of cadmium significantly decreased the content of the determined dyes in wheat (Table 1). The average content of chlorophyll a and b in the control plants amounted to about 2.37 mg·g⁻¹ of fresh matter. After adding a 5 mM dose of cadmium, a decrease in the content of chlorophyll a by 34%, chlorophyll b by 37% and carotenoids by 29% with respect to the control plant was observed in wheat (Table 1). The amount of chlorophyll a, b and carotenoids in the examined plant, when the highest dose and mineral fertilization were applied, constituted respectively 73%, 68% and 78% with respect to the control plant (Table 1). Chen and Kreeb [18] recorded over a twofold decrease in chlorophyll in maize under the influence of heavy metals as compared to the control. Hou et al. obtained a decreased amount of chlorophyll a by 46%, chlorophyll b by 32% and carotenoids by 48% in *Lemna minor* after the application of a 20 mg·dm⁻³ dose [5]. Erdei et al. [12] recorded a 60% decrease in the content of chlorophyll in barley after the application of cadmium. In the carried out studies, a stimulating effect of the lowest dose of cadmium – 0.025 mM, on the content of the determined photosynthetic dyes in spring wheat, was also observed. A 5% increase was noticed in the content of chlorophyll b, and a 10% increase in the content of carotenoids in wheat at the shooting stage after the application of 0.025 mM of cadmium with respect to their concentration in the studied plant in the phase of two cotyledones (Table 1). An increased amount of chlorophyll b in stonecrop (*Sedum*) after the application of Cd in the dose of 10⁻⁴ M was obtained by Zhou and Qiu [19]. The studies carried out by Nikolić et al. [4] showed, in poplar growing in a 10⁻⁴ M Cd medium, an increase in the content of chlorophyll b by 49%, and carotenoids by 10% in relation to the control plant. Based on the value of the correlation coefficient, a significant negative correlation relationship was observed between the content of photosynthetic pigments (chlorophyll a and b and carotenoids) and the concentration of cadmium in the leaves of spring wheat (Fig. 1a, b).

Table 1

Toxic impact of cadmium on the content of photosynthetic pigments
in leaves of spring wheat (*Triticum vulgare*)

Day	Dose of Cd [mM]									
	Control	NPK	NPK +0.025	NPK + 0.05	NPK + 0.5	NPK + 5	0.025	0.05	0.5	5
Chlorophyll a [$\text{mg}\cdot\text{g}^{-1}$ f.m.] (% of control)										
7	1.59 ± 0.57	1.48 ± 0.33	1.39 ± 0.12	1.40 ± 0.08	1.54 ± 0.18	1.24 ± 0.01	1.31 ± 0.11	1.47 ± 0.04	1.37 ± 0.03	1.12 ± 0.03
14	1.60 ± 0.11	1.77 ± 0.18	1.46 ± 0.01	1.27 ± 0.07	1.53 ± 0.15	1.15 ± 0.14	1.40 ± 0.10	1.39 ± 0.10	1.32 ± 0.03	1.10 ± 0.02
21	1.77 ± 0.06	1.87 ± 0.01	1.30 ± 0.06	1.52 ± 0.03	1.43 ± 0.08	1.32 ± 0.06	1.21 ± 0.01	1.10 ± 0.02	1.29 ± 0.02	1.08 ± 0.08
28	1.67 ± 0.06	1.91 ± 0.01	1.67 ± 0.22	1.20 ± 0.23	1.12 ± 0.01	1.11 ± 0.12	1.36 ± 0.01	1.33 ± 0.21	1.21 ± 0.25	1.05 ± 0.02
Average	1.66 ± 0.20 (100)	1.76 ± 0.13 (106)	1.46 ± 0.10 (88)	1.38 ± 0.10 (83)	1.40 ± 0.11 (84)	1.21 ± 0.08 (73)	1.32 ± 0.06 (80)	1.32 ± 0.09 (80)	1.26 ± 0.08 (76)	1.09 ± 0.04 (66)
LSD _{0.05} day – 0.112; dose – 0.232;										
Chlorophyll b [$\text{mg}\cdot\text{g}^{-1}$ f.m.] (% of control)										
7	0.62 ± 0.15	0.74 ± 0.13	0.49 ± 0.01	0.64 ± 0.05	0.55 ± 0.09	0.52 ± 0.02	0.55 ± 0.02	0.56 ± 0.04	0.57 ± 0.05	0.46 ± 0.01
14	0.63 ± 0.11	0.65 ± 0.19	0.60 ± 0.03	0.56 ± 0.01	0.57 ± 0.11	0.48 ± 0.04	0.57 ± 0.05	0.56 ± 0.11	0.54 ± 0.04	0.45 ± 0.02
21	0.78 ± 0.14	0.95 ± 0.03	0.65 ± 0.02	0.57 ± 0.17	0.54 ± 0.02	0.49 ± 0.07	0.58 ± 0.04	0.53 ± 0.03	0.54 ± 0.05	0.46 ± 0.02
28	0.80 ± 0.03	0.89 ± 0.09	0.75 ± 0.16	0.53 ± 0.06	0.46 ± 0.01	0.45 ± 0.03	0.58 ± 0.01	0.49 ± 0.07	0.47 ± 0.02	0.44 ± 0.01
Average	0.71 ± 0.11 (100)	0.81 ± 0.11 (114)	0.62 ± 0.06 (87)	0.59 ± 0.07 (83)	0.53 ± 0.06 (75)	0.48 ± 0.04 (68)	0.57 ± 0.03 (80)	0.54 ± 0.06 (76)	0.53 ± 0.04 (75)	0.45 ± 0.02 (63)
LSD _{0.05} day – 0.098, dose – 0.118										
Carotenoids [$\text{mg}\cdot\text{g}^{-1}$ f.m.] (% of control)										
7	0.59 ± 0.17	0.61 ± 0.07	0.54 ± 0.05	0.51 ± 0.06	0.58 ± 0.06	0.46 ± 0.01	0.49 ± 0.04	0.57 ± 0.01	0.54 ± 0.03	0.44 ± 0.03
14	0.60 ± 0.04	0.66 ± 0.07	0.57 ± 0.01	0.50 ± 0.01	0.56 ± 0.05	0.48 ± 0.03	0.56 ± 0.04	0.55 ± 0.02	0.58 ± 0.02	0.46 ± 0.01
21	0.72 ± 0.01	0.74 ± 0.01	0.55 ± 0.01	0.61 ± 0.01	0.59 ± 0.03	0.54 ± 0.02	0.50 ± 0.01	0.43 ± 0.02	0.54 ± 0.02	0.46 ± 0.01
28	0.62 ± 0.02	0.80 ± 0.07	0.74 ± 0.11	0.52 ± 0.10	0.50 ± 0.01	0.46 ± 0.04	0.57 ± 0.01	0.54 ± 0.08	0.50 ± 0.06	0.42 ± 0.04
Average	0.63 ± 0.06 (100)	0.71 ± 0.06 (113)	0.60 ± 0.04 (95)	0.55 ± 0.05 (87)	0.56 ± 0.03 (89)	0.49 ± 0.03 (78)	0.53 ± 0.03 (84)	0.52 ± 0.03 (82)	0.52 ± 0.03 (82)	0.45 ± 0.02 (71)
LSD _{0.05} day – 0.073, dose – 0.103;										

Table 2

Intensities of CO₂ assimilation, transpiration and the photosynthetic efficiency of water use in wheat growing in soil with various doses of cadmium

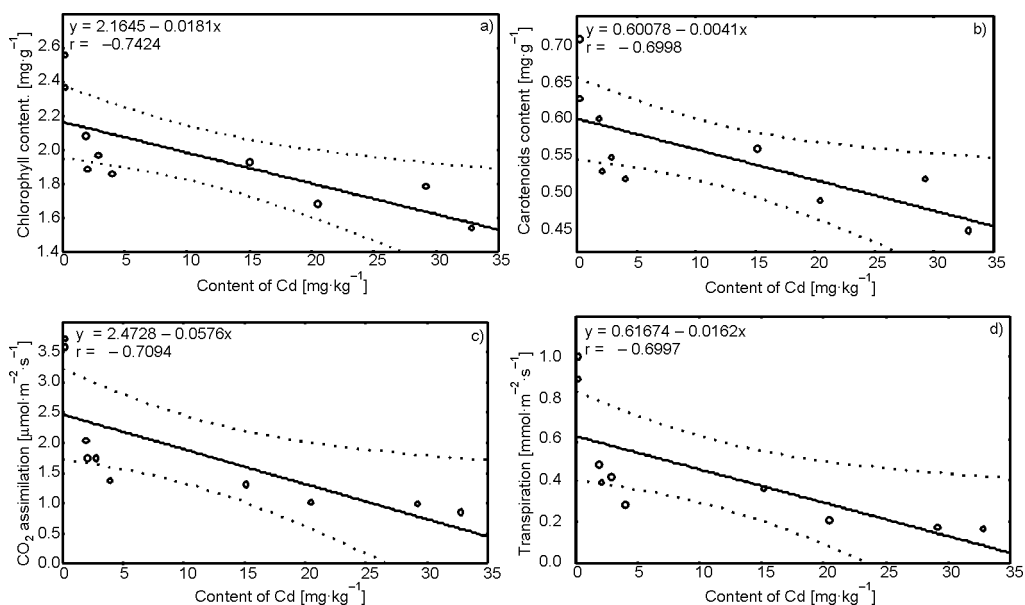
Day	Combination in experiment; dose of Cd [mM]									
	Control	NPK	NPK +0.025	NPK + 0.05	NPK + 0.5	NPK + 5	0.025	0.05	0.5	5
CO ₂ assimilation ($\mu\text{mol} \cdot \text{m}^{-2} \cdot 7\text{s}^{-1}$) (% of control)										
7	4.53 ±0.51	4.49 ±0.39	2.29 ±0.20	1.83 ±0.15	2.01 ±0.23	1.43 ±0.17	1.97 ±0.09	1.52 ±0.40	1.44 ±0.21	1.17 ±0.13
14	4.03 ±0.22	3.68 ±0.79	2.48 ±0.39	2.27 ±0.35	1.15 ±0.19	1.12 ±0.04	2.16 ±0.31	1.56 ±0.27	1.02 ±0.09	0.92 ±0.13
21	3.25 ±0.53	3.32 ±0.21	1.56 ±0.19	1.74 ±0.36	1.11 ±0.08	1.03 ±0.28	1.62 ±0.08	1.21 ±0.25	1.05 ±0.14	0.94 ±0.09
28	3.11 ±0.41	2.88 ±0.38	1.79 ±0.06	1.15 ±0.10	1.03 ±0.08	0.59 ±0.07	1.27 ±0.17	1.19 ±0.11	0.56 ±0.14	0.43 ±0.10
Average	3.73 (100)	3.59 (96)	2.04 (55)	1.75 (47)	1.33 (36)	1.04 (28)	1.76 (47)	1.37 (37)	1.02 (27)	0.87 (23)
LSD _{0.05} day – 0.589, dose – 0.778										
Transpiration [$\text{mmol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$] (% of control)										
7	1.21 ±0.09	1.06 ±0.03	0.66 ±0.06	0.57 ±0.03	0.55 ±0.10	0.37 ±0.15	0.46 ±0.10	0.37 ±0.07	0.32 ±0.04	0.28 ±0.06
14	1.17 ±0.09	0.87 ±0.07	0.45 ±0.06	0.50 ±0.06	0.32 ±0.03	0.23 ±0.06	0.51 ±0.06	0.29 ±0.04	0.18 ±0.02	0.16 ±0.04
21	0.95 ±0.07	0.89 ±0.12	0.47 ±0.10	0.43 ±0.07	0.25 ±0.05	0.18 ±0.03	0.39 ±0.03	0.30 ±0.03	0.11 ±0.02	0.12 ±0.04
28	0.71 ±0.09	0.76 ±0.04	0.35 ±0.04	0.19 ±0.07	0.31 ±0.06	0.07 ±0.03	0.23 ±0.07	0.21 ±0.04	0.13 ±0.05	0.11 ±0.03
Average	1.01 (100)	0.90 (89)	0.48 (47)	0.42 (41)	0.36 (35)	0.21 (21)	0.40 (39)	0.29 (29)	0.18 (18)	0.17 (17)
LSD _{0.05} day – 0.134, dose – 0.241										
Photosynthetic efficiency of water use [$\mu\text{mol} \cdot \text{mmol}^{-1}$]										
7	3.74	4.23	3.47	3.21	3.65	3.86	4.28	4.11	4.50	4.18
14	3.44	4.23	5.51	4.54	3.59	4.87	4.23	5.37	5.66	5.75
21	3.42	3.73	3.32	4.05	4.44	5.72	4.15	4.03	9.54	7.83
28	4.38	3.78	5.11	6.05	3.32	8.42	5.52	5.67	4.31	3.91

Malinowska [20] and Łukasik et al. [21] also noticed a negative significant correlation between the content of cadmium and chlorophyll a and b in leaves. By accumulating in chloroplasts, cadmium destroys the structure of these organelles and thus inhibits the synthesis of photosynthetic pigments [3, 7, 8]. It can also cause damage to the membranes of chloroplasts and thylakoids by increased production of free radicals [22].

Table 3

Activities of antioxidant enzymes in wheat plants depending on the Cd²⁺ doses added to soil

Stages of wheat development	Term of analysis (day)	Combination in experiment; dose of Cd [mM]										LSD _{0.05}
		Control	NPK	NPK +0.025	NPK +0.05	NPK +0.5	NPK +5	0.025	0.05	0.5	5	
Catalase activity (CAT) [$\mu\text{M H}_2\text{O}_2\cdot\text{g}^{-1}\text{ f.m.}\cdot\text{min}^{-1}$]												
Two leaf stage	7	0.337	0.341	0.341	0.371	0.420	0.786	0.346	0.376	0.439	0.796	0.004
Shooting	14	0.464	0.459	0.468	0.498	0.561	1.201	0.488	0.468	0.551	1.274	0.014
	21	0.332	0.322	0.346	0.424	0.561	1.006	0.351	0.424	0.561	1.089	0.007
	28	0.283	0.302	0.327	0.337	0.434	0.854	0.327	0.341	0.429	0.849	0.003
Peroxidase activity (POX) [$\mu\text{M purpurogaline}\cdot\text{g}^{-1}\text{ f.m.}\cdot\text{min}^{-1}$]												
Two leaf stage	7	0.443	0.502	0.513	0.858	0.963	1.080	0.528	0.875	1.050	1.163	0.002
Shooting	14	0.237	0.267	0.299	0.492	0.547	0.585	0.278	0.501	0.580	0.614	0.002
	21	0.594	0.605	0.708	1.114	1.284	1.478	0.768	1.177	1.269	1.535	0.002
	28	0.682	0.697	0.803	1.237	1.576	1.606	0.859	1.254	1.587	1.634	0.004
Superoxide dismutase activity (SOD) [$\text{U}\cdot\text{g}^{-1}\text{ f.m.}\cdot\text{min}^{-1}$]												
Two leaf stage	7	106.5	104.6	112.4	135.6	166.6	179.2	116.2	131.7	166.6	183.5	4.472
Shooting	14	54.2	58.1	67.8	62.0	77.5	89.4	56.2	83.3	102.7	104.2	5.750
	21	112.4	118.2	122.1	141.4	166.6	172.5	125.3	135.6	176.3	188.4	6.846
	28	34.8	40.6	48.4	67.8	77.5	78.7	36.8	63.9	58.1	66.2	6.404

Fig. 1. Dependences of the contents of photosynthetic pigments ($\text{mg}\cdot\text{g}^{-1}$ of fresh matter, a, b), CO₂ assimilation (c) and transpiration (d) on the content of cadmium in leaves of spring wheat

A significant decrease was observed in the intensity of the examined physiological processes both at the stage of two cotyledones and in the phase of shooting in spring wheat growing in a soil with various doses of cadmium added. The highest decrease in the intensity of CO₂ assimilation and transpiration was recorded after a maximum dose of cadmium (5 mM) had been applied. The intensity of the photosynthesis process in such cultivation conditions decreased by 77%, whereas that of transpiration by 83% in relation to the control plant (Table 2). The decrease in the intensity of photosynthesis and transpiration can be related to the disturbances in functioning of the photosynthetic apparatus of the plants, the decrease in turgor, the inhibition of the transport of electrons in the process of photosynthesis and the decrease in the activity of carboxylase RuBP [4, 5, 7].

Photosynthetic effectiveness of the use of water is often a decisive index of productivity of plants under stress conditions [23]. The calculated index differed depending on the applied doses and of the growth stage of the plant. The increase in the photosynthetic effectiveness was observed in all stages of the experiment. Its highest 2.5-fold increase with respect to the control plants was obtained after the application of the dose of 0.5 and 5 mM at the shooting stage (21st day of studies) (Table 2). This results, first of all, from the low intensity of transpiration. Similar reactions of plants to the influence of heavy metals were recorded by Malinowska and Smolik [24]. As results from the value of the correlation coefficient, close relationships between the defined physiological processes and the concentration of cadmium in leaves of spring wheat were observed (Fig. 1c, d). The values of the correlation coefficients r for CO₂ assimilation and transpiration amounted to -0.7094 and -0.6697 . Malinowska [20] reported a negative significant correlation between the intensity of photosynthesis and the content of cadmium in the leaves of plants.

The activity of catalase in wheat growing in the control soil in the phase of two leaves amounted to $0.337 \text{ mg H}_2\text{O}_2 \cdot \text{g}^{-1}$ of fresh matter $\cdot \text{min}^{-1}$. The enzyme reached the highest activity in all the combinations at the stage of shooting on the 14th day of the experiment (Table. 3).

The applied doses of cadmium (0.025–5 mM) caused a significant increase in the activity of catalase in all the examined growth phases of wheat. In the phase of shooting (21st day of measurement) the applied dose 5 mM + NPK caused an increase in the activity of catalase by 202%, whereas the highest dose of cadmium without fertilizers resulted in an increase by 228% with respect to the control plant (Table 3).

In both phases of wheat growth an increase in the activity of peroxydase was observed with an increase in the dose of cadmium in soil. A significant growth in the activity of this enzyme at an approximate level was observed during the whole experiment. The most distinct stimulation was recorded in the phase of two leaves, i.e. by 19%, 97%, 137% and 162% respectively for the doses of cadmium exceeding permissible amount of metal in the soil.

A significant stimulating effect of all the applied concentrations of NPK and cadmium salt on the activity of superoxide dismutase in the examined growth phases of wheat was also noticed. The enzyme reached the lowest activity in the phase of shooting during the last measurement (Table 3). The observed increase in the activity of the enzymes can be caused by an increase in the production of reactive forms of oxygen in plants. The activation of catalase in small radish under the influence of CdCl_2 applied in the concentrations from 0.25 to 1 mM is reported by Vitória et al. [25]. Hegedüs et al. [26] showed that the addition of cadmium in concentrations ranging from 0.1 mM to 0.3 mM had a stimulating effect on the activity of peroxydase in wheat. A significant increase in the activity of peroxydase was observed in the leaves of the examined plants; whereas no significant changes in its activity were noticed in the roots with respect to the control plants. Saffar et al. [27] found that cadmium at various concentrations (50, 85 i 100 μM of CdCl_2) decreased the activity of catalase in seedlings of *Arabidopsis thaliana*, while an increase in the activity of peroxydase was observed. The experiment carried out by Ammar et al. [28] showed an increase in the activity of superoxide dismutase in tomato plants upon increasing concentration of cadmium salt (1–50 μM Cd^{2+}).

4. CONCLUSIONS

The applied doses of cadmium (0.05–5 mM) significantly reduced the content of defined photosynthetic pigments in all the studied phases of growth of spring wheat.

Upon increasing the doses of cadmium, the intensity of assimilation of CO_2 and transpiration in wheat significantly decreased while the index of use of water in photosynthesis increased.

The content of chlorophyll a and b and carotenoids significantly decreased upon increasing concentration of cadmium in the leaves of spring wheat.

Cadmium had a clear stimulating effect on the activity of catalase, peroxydase and superoxide dismutase in the studied growth phases of spring wheat.

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APPRAISE OF CONSEQUENCES OF EROSION PROCESSES OCCURRING IN THE SKAWA RIVER SECTOR

Erosive processes have been evaluated in a sector of the Skawa river characterized by high pliability to erosion (proportion between the bend radius and the river channel width equals on the average 6.5). Within two years, channel erosion caused by 6 freshets was investigated with flows Q within the range of probability of waters from 20% to 50%. Bank and bottom erosion as well as transportation of the bed material and material from falls of bank slopes were found to occur. Intensity of this transportation was calculated based on Bagnold's equation. The calculated value of transported bed load was comparable with that obtained from direct measurements. The effects of transportation were also reflected by changes of the grain size distributions after passage of a freshet wave. Bank erosion was the dominating process that changed the river channel shape. It was found that in the examined sector the retreat of the bank slope proceeded at the rate of 1.20 m/year.

1. INTRODUCTION

Erosion in mountain rivers is a process proceeding permanently; direction of its activity and intensity depends on such factors as water flow, gradient of the river channel, regime of water flow, bed load and frequency of its migration. Erosion of the river bed begins when transportation of bottom material prevails over the amount of material obtained from the upper parts of the river, and bank erosion is manifested by shifting of banks and channel migration.

River dynamics is the problem of interest of hydrotechnicians and geomorphologists [1–5]. Many authors investigated channel processes against the background of hydraulic processes prevailing in water flows [6–8]. A considerable amount of papers describe effects of freshets and their influence on erosive phenomena, bottom material

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transportation and its accumulation [9–12]. In frequently expressed opinion, transport of bottom material is a factor regulating relations between all channel processes. For example: increase in the amount of transported material causes increase in bank erosion, whereas, when transportation intensity decreases bottom erosion or bed load accumulation may increase [13–16]. It results from the analysis of a number of investigations that erosion and geometry of the river channel are closely related: intensity of bank erosion is a function of the relation of the channel width and radius of its curvature. Occurrence of erosive processes leads also to disturbance of hydrodynamic stability of the flow even if they occur only in some sectors. Local lack of hydrodynamic balance causes a consequent destabilization of the channel in adjacent sectors. Erosion investigated in the sector of the River Skawa located in the upper part of its course is an example illustrating this type of river activity.

2. CHARACTERISTICS OF THE STUDIED SKAWA RIVER SECTOR

The Skawa river, 91 km long with the watershed area A of 1187 km² is one of the biggest right-bank mountain tributaries of the Wisła river. It takes its sources in the sandstones and Magurian slates in the transitional area (region) between Babia Góra Range and Sieniawa Gate. The springs rise from the north-west slope of the main Łysa Góra massifs 700 m above sea level. The Skawa Valley and its tributaries are narrow deeply indented with lots of gorges of big drop. There are considerable denivelations between the ridges and beds of the valleys often reaching up to 600 m. The investigated sector (Fig. 1) is localized near the Wadowice water gauge section.



Fig. 1. Part of a studied sector of the Skawa river

In field research, the geological structure of the bed within the investigated stretch was estimated based on the exposed ground visible in the bottom and on the scarps.

Up to the depth of 3.0–4.5 m it is built of gravel containing thick pebbles, the overlaying layer consists of alluvial river deposits represented by 2.0–3.0 m thick sand clay and gravel clay formations covered with 0.20–0.30 m soil layer.

3. FRESHETS

The probable and daily water discharges for the investigated Skawa river sector were obtained from observations carried out by the Institute of Meteorology and Water Management (IMGW), the Wadowice gauging station which is situated in the immediate vicinity of the investigated stretch. Six floods were observed in the researched period from 2004 to 2005 (Fig. 2). Water discharge Q ranged from $62.5 \text{ m}^3\text{s}^{-1}$ (November 24,

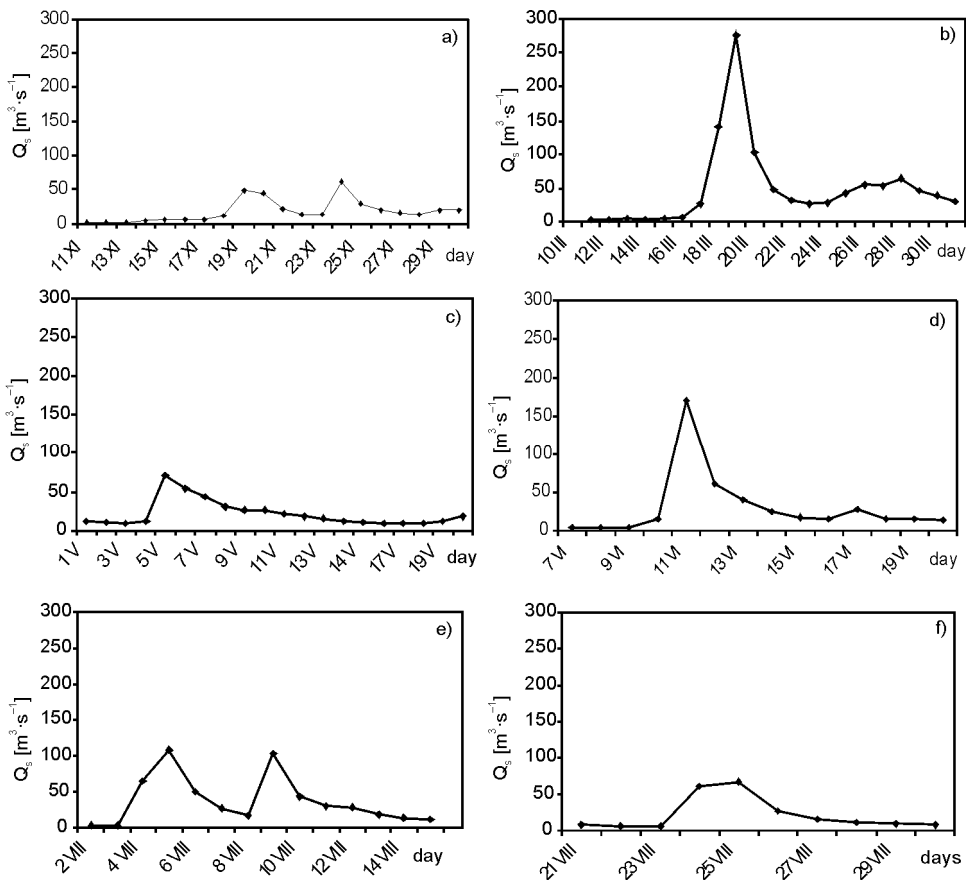


Fig. 2. Water discharges for the Wadowice gauging station:

- a) freshet of 11–30.09.2004, b) freshet of 11–31.03.2005, c) freshet of 01–20.05.2005, d) freshet of 07–20.06.2005, e) freshet of 01–15.08.2005, f) freshet of 21–31.08.2005

2004) which corresponds to the discharge of probable occurrence lower than $Q_{50\%}$ to $Q = 276 \text{ m}^3 \cdot \text{s}^{-1}$ (March 19, 2005) which corresponds to a discharge of probable occurrence between $Q_{20\%}$ and $Q_{50\%}$. The latter water discharge approximated a medium high stage. In Table 1, mean characteristic water discharge values and probable discharge values for the Wadowice gauging station are presented.

Table 1

Mean characteristic water discharge in the river Skawa sector and probable discharge for the Wadowice gauging station

Catchment area [km ²]	Medium-low stage [m ³ ·s ⁻¹]	Annual average [m ³ ·s ⁻¹]	Medium-high stage [m ³ ·s ⁻¹]
838	3.04	8.50	250
Water flow with percentage probability of appearance [m ³ ·s ⁻¹]			
1%	20%		50%
1043	385		190

4. CHARACTERISTICS OF CROSS-SECTIONS AND AN ATTEMPT TO ESTIMATE THE INTENSITY OF LATERAL AND DEEP-SEATED EROSION

In August 2004, four cross-sections, schematically presented in Fig. 3, were measured in the analyzed Skawa river sectors. The I-I Section was situated at 21 + 400 km of the water course (measured from its mouth) and was the lowest measured cross-section. The other sections were localized at a distance of $l = 120$ m above the base section. Special measurements were taken on the right river bank whose height h_p approaches 4.0 m (metal sounds were set into scarps to read the thickness of the eroded material). All the surveyed sections had the scarp slope close to the natural slope gradient and an almost vertical part of the scarp up to 2.50 m height. The shape of all the sections was trapezium like with the maximum depression in the central part of the channel or shifted towards the eroded bank. The proportion between the bend radius and the channel width r/b for this stretch was 6.5 which indicates high susceptibility to erosion [11].

The sections were the point of reference for the measurements taken in the years to follow. Survey and field research conducted after floods in November 2004 as well as in May and August 2005 did not demonstrate measurable changes in the topography of the river bed as the observed discharges were not able to move the bed material. Shear stress was decidedly lower than the critical stress which, when exceeded, sets bed rubble in motion. Thus, it can be stated morphologically inactive. As regards the banks, the changes observed were minimal and the metal sounds showed the maximum change $\Delta b_p = 0.03$ m. The changes did not concern all surveyed height of the scarp but occurred locally at various heights above water level which seems to indi-

cate that they were caused by other reasons independent of the flowing water. Most probably they resulted from a combination of various factors such as destructive effect of rain drops, eolic erosion, and animal activity, swelling and shrinking of ground causing pebbles to come off from scarps. The disconnected material accumulated at the foot of the vertical bank.

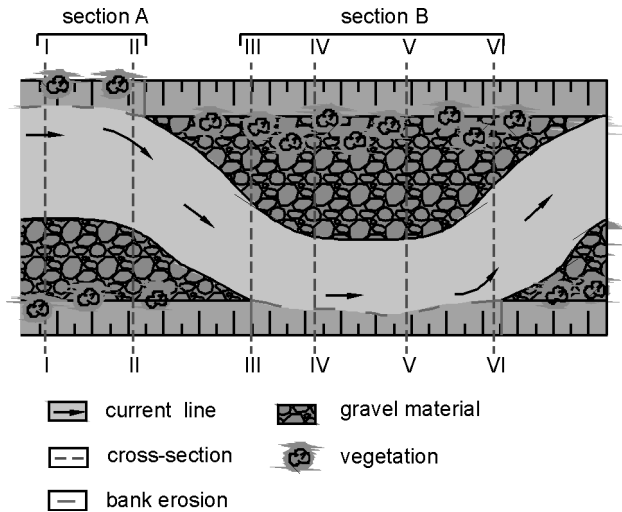


Fig. 3. Outline of the measuring sector

The spring flood was most active morphologically and caused lateral bank migration. The displacement b_p ranged from 0.13 m to 0.15 m. The highest displacement was noticed in section II–II (Fig. 4b) $\Delta b_p > 1.5$ m in the bed and ca. 0.8 m at the level of approximately 1 m.

The smallest changes were found in the closing section of the investigated stretch IV–IV (Fig. 4d) and Δb_p did not exceed 0.1 m. Nevertheless it should be mentioned that the changes observed in this section did not occur in the entire bank but only in its part up to ca. 1.2 m. The lateral erosion was accompanied by bed erosion, the changes were observed in bed ordinate and reached $\Delta h_d = 0.2$ m at the maximum. In section III–III (Fig. 4c) the bed erosion was more intensive as (close to the measure point) it formed an erosion trough about 8 m long, 2 m wide and the mean depth of 0.4 m. It was cut out along a wooden obstruction, namely a tree trunk ca. 2 m away from the bank. In cross-sections from I–I (Fig. 4a) to III–III, a superstructure of gravel bar was observed at the opposite cambered bank, $\Delta h_1 = 0.1$ m at the maximum.

Variability of material fractions in the crosswise profile was its characteristic feature. The thickest material was found close to the current and as moving towards the opposite direction of the eroded bank it was becoming smaller and smaller. In IV–IV

section, the upper part of the bar was locally washed away (over the area of 15 m long, up to 20 m wide an up to 0.08 m thick layer was carried away).

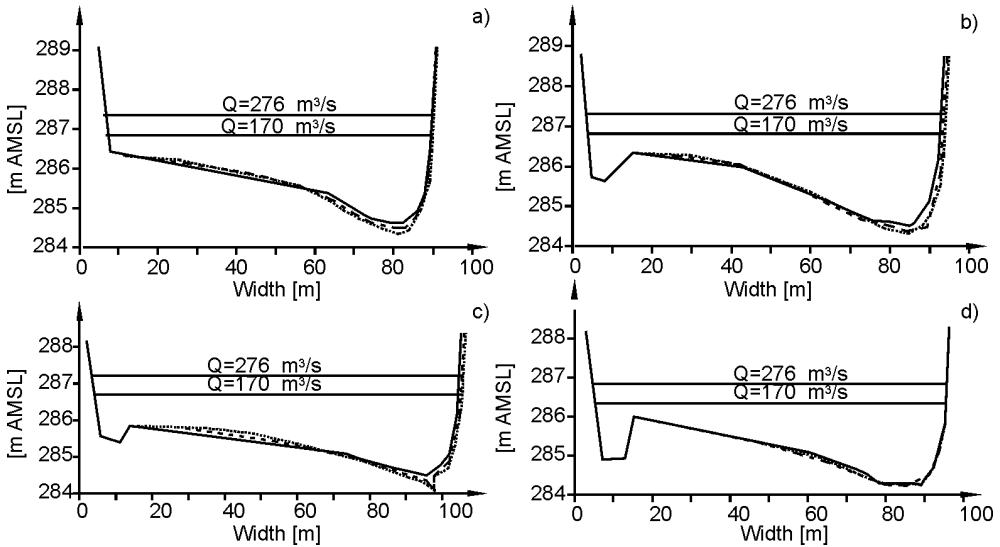


Fig. 4. Cross-sections measured on the Skawa river: a) sector A, cross-section I–I, b) sector A, cross-section II–II, c) sector B, cross-section III–III, d) sector B, cross-section IV–IV; solid lines – measured in August 2004, dashed lines – in March 2005, dotted lines – in June 2005

The estimated volume V_1 of the material eroded from the investigated sector was 366 m^3 , and that deposited within the point bar $V_2 = 155 \text{ m}^3$. The shear stress and the individual stream power were calculated for the conditions in the channel during a freshet. The values were $\tau = 56.6 \text{ N}\cdot\text{m}^{-2}$, $\omega = 22.44 \text{ kg}\cdot\text{m}^{-1}\cdot\text{s}^{-1}$, respectively. The value of the shear stress was 1.9-fold higher than the limit value ($\tau_{cr} = 39.43 \text{ N}\cdot\text{m}^{-2}$) which is necessary to set the bed material in motion. The above calculations indicate that both the bed material and that torn off from the scarps were transported throughout the researched river stretch. The existing stream power was sufficient to set in motion even the biggest grains found when sampling grain size composition. The second flood which caused some changes in the topography of the river bed and in the shape of the river banks was observed on 11.06.2005 and the water discharge Q recorded on that day was $170 \text{ m}^3\cdot\text{s}^{-1}$. Shear stress and stream power were $\tau = 41.15 \text{ N}\cdot\text{m}^{-2}$, $\omega = 11.24 \text{ kg}\cdot\text{m}^{-1}\cdot\text{s}^{-1}$, respectively. The calculated values indicate that the stress in the river bed and the stream power were high enough to transport bed rubble, but smaller than those observed in May. The transportation ability of the channel was lower than that found during spring flood.

The layer of the material detached from the bank did not exceed $\Delta b_p = 0.8 \text{ m}$ and was recorded in III–III section. Within the cross-sections I–I and III–III, further lowering of the bed grade line by 0.10 m was observed at the maximum. In the closing sec-

tion IV–IV, the mean increase of the bed layer was 0.15 m at the area of the right bank while below this section an additional layer was found on the existing meander point bar. No significant changes were found in this section as regards the shape of the bank scarp ($\Delta b_p < 0.02$ m), a further washing away of the gravel point bar was noted ranging from 0.04 m to 0.07 m. The estimated volume V_1' of the material detached from the bank scarp and eroded from the channel bed was 121 m³, while the volume V_2' of the material deposited on the point bar approximated 77 m³.

5. GRAIN SIZE COMPOSITION OF THE BED MATERIAL

The grain size composition of the rubble was determined for the II-II section in each survey which helped to demonstrate how the bed material changed after the flood. Table 2 shows the selected diameters of grains and the characteristics of the grain size distribution such as domination coefficient $C_d = (d_{95} \cdot d_{10}) / d_{50}^2$, standard deviation $\delta = (d_{84} / d_{16})^{0.5}$ separation degree $\mu = d_{60} / d_{10}$ and heterogranulation index $\varepsilon = d_{90} / d_5$.

Table 2

Selected diameters of grains and the characteristics of the grain size distribution

Date	d_m [m]	d_{10} [m]	d_{16} [m]	d_{50} [m]	d_{60} [m]	d_{84} [m]	d_{90} [m]	μ	ε	δ	Cd
August 2004	0.057	0.020	0.025	0.053	0.072	0.102	0.110	3.6	23	2.3	0.82
March 2005	0.054	0.013	0.020	0.052	0.060	0.090	0.100	4.6	22	2.6	0.53
June 2005	0.047	0.019	0.019	0.045	0.052	0.072	0.080	5.2	20	2.7	0.49

An analysis of grain size distribution shows changes in grain size composition depending on the varying hydrodynamic conditions during flood. One can notice a reduction of the mean diameter by $\Delta d = 0.01$ m in June 2005 compared with the initial grain-size composition. Concurrently a significant increase of small fractions percentage was observed at simultaneous decreasing by $\Delta p_i = 17\%$ of percentage of bigger sizes fractions $d > 0.08$ m in a sample of material.

6. INTENSITY OF BED LOAD TRANSPORT

Having at disposal geometrical data and well defined hydraulic conditions in the stretch under research one can calculate the intensity of bed load transport being the effect of flood. In order to estimate the intensity of this transport i_b we used the following formula according to Bagnold [17]:

$$i_b = (\omega - \omega_0)^{3/2} h^{-2/3} d^{-1/2}$$

To eliminate the diversity in size the author suggested the following unidimension form of the equation

$$\frac{i_b}{(i_b)_*} = \left(\frac{\omega - \omega_0}{(\omega - \omega_0)_*} \right)^{3/2} \left(\frac{h}{h_*} \right)^{-2/3} \left(\frac{d}{d_*} \right)^{-1/2}$$

The values with an index are arbitrarily chosen basing on the results available from field and laboratory research and are as follows:

$$(i_b)_* = 0.1 \text{ kg} \cdot \text{m}^{-1} \cdot \text{s}^{-1}, \quad (\omega - \omega_0)_* = 0.5 \text{ kg} \cdot \text{m}^{-1} \cdot \text{s}^{-1},$$

$$h_* = 0.1 \text{ m}, \quad d_* = 1.1 \cdot 10^{-3} \text{ m}$$

Calculations were made for the II-II cross-section taking into consideration all rubble fractions. By multiplying the intensity of bed load transport by the duration of the given filling and the width of the transport belt we obtained the total weight of the transported material which was converted into volume. The result obtained and the hydrodynamic data are plotted in Table 3.

Table 3

Weight and volume of the transported material

Date	$i_b \text{ max}$ [kg·m ⁻¹ ·s ⁻¹]	G [kN]	V [m ³]	V' [m ³]
March 2005	0.34	6039.1	232	211
June 2005	0.12	1496.5	57	44

The results calculated according to Bagnold's equation were correspondent with those obtained in field research. The volume of the transported bed material acquired using the equation and that obtained in direct survey are comparable.

7. RECAPITULATION OF RESULTS AND CONCLUSIONS

The applied method of survey enabled estimation of morphological changes in the river channel caused by flood.

The present study proved that processes such as destructive action of rain drops, eolic erosion, activity of animals, heaving and shrinking of ground in rainy and dry weather are of secondary importance compared with the action of flood.

Within the researched sector, a dominating process which changed the shape of the channel was bank erosion, whose intensity depends on the volume of water discharge and its duration. Nevertheless, no linear correlation was found between the volume of the discharged water and the intensity of the occurring processes.

Irrespective of bank erosion, a significant manifestation of flood activity is bed material transport in the channel which, no matter how intensive, causes changes in grain size distribution after the flood.

The mean rate of bank scarp withdrawal was 1.20 m per year in the researched stretch.

SYMBOLS

b	– width of channel, m
b_p	– width of erosion belt on a right bank, m
$d_{10\%, 50\%}$	– the size of sediment which respectively percent of the sample is finer
d_i	– diameter of a grain fraction i
G	– weight, kN
h_p	– height of a right scarp, m
p_i	– percentage of fraction i
r	– radius of meander, m
i_b	– intensity of bed load transport, $\text{kg}\cdot\text{m}^{-1}\cdot\text{s}^{-1}$
R_h	– hydraulic radius, m
Q	– discharge, $\text{m}^3\cdot\text{s}^{-1}$
$Q_{50\%}$	– water flow with 50% probability of appearance, $\text{m}^3\cdot\text{s}^{-1}$
$Q_{20\%}$	– water flow with 20% probability of appearance, $\text{m}^3\cdot\text{s}^{-1}$
V	– volume, m^3
V'	– difference between bulk of dead load accumulated and bed material eroded along the studied sector, m^3
\bar{v}	– mean cross-sectional velocity of water, $\text{m}^3\cdot\text{s}^{-1}$
C	– Chezy coefficient
I	– water surface slope
Δb_p	– thickness of the eroded bank layer, m
Δb_d	– difference of river bed elevation, m
Δb_1	– difference of bar elevation, m
τ	– shear stress, $\text{N}\cdot\text{m}^{-2}$
τ_{cr}	– critical shear stress, $\text{N}\cdot\text{m}^{-2}$
ω	– stream power, $\text{N}\cdot\text{m}^{-1}\cdot\text{s}^{-1}$

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PILOT STUDY ON CHEMICAL INDUSTRIAL WASTEWATER IN TERTIARY TREATMENT WITH BIOFILM FOR WASHING BELTS

The biochemical characteristics of chemical secondary effluent of the wastewater treatment plant of Jilin Chemical Industry Corporation have higher residual concentration of COD_{Cr} and $\text{NH}_3\text{-N}$, and lower residual concentration of BOD_5 and alkalinity. These biochemical characteristics of chemical secondary effluent in tertiary treatment were studied with a pilot system of biological contact aerators (BCAs) to meet national discharged limits and requirements for washing belts, particularly to meet national limits of ammonia and benzene substances, etc. in the air of a workshop. The highest removal efficiency was obtained in the BCAs system and a scientific basis of reference was provided for reforming the system of pulse flocculated clarifier which can constitute a new approach in tertiary wastewater treatment for washing belts.

1. INTRODUCTION

Jilin Chemical Industry Corporation (JCICWTP) adopts the anoxic/oxic (A/O) process in secondary treatment and PFC process in tertiary treatment. As the current loading of wastewater is $6000 \text{ m}^3/\text{h}$, the wastewater needs to be treated to meet national discharged limits and requirements for washing belts, especially to meet national limits of ammonia and benzene substances in the air of a workshop. The wastewater characteristics are very complicated, it contains a great deal of non-biodegradable organic matter such as benzene, pesticides, organic agrochemicals, petroleum processing waste, complex aromatic substances, epoxy resin, dyestuff, intermediate pigment, etc. The effluent $\text{NH}_3\text{-N}$ and COD_{Cr} concentration in the A/O process did not meet national limits on effluent discharged because of the more significant organic

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content of non-biological substance in the influent. The PFC was used for treating secondary effluents of the A/O process, according to the results of previous studies; the removal efficiencies of COD_{Cr} and $\text{NH}_3\text{-N}$ were inadequate in the PFC.

As operating parameters and influent fluctuations affect the performance of the A/O system [1, 2], nitrogen and carbon removal is not at a satisfactory level under the traditional mode of A/O operation [3]. The traditional operation of the pulse-flocculated system often fails to attain optimum results for the removal of solids, carbonaceous organic matter, and nutrients. Moreover, stricter regulations on wastewater effluents, technical limitations on treatment site, and energy consumption issues have heightened the importance of modifying biological wastewater processes using biochemical film processes [4].

BCAs and biological aerated filters (BAFs) are biofilm systems used mainly for the tertiary treatment of wastewater [5]. When fibre spacers or granular media are used, the system is capable of removing organic matter, suspended solids, and nitrogen from wastewater at the same time; hence, there is no need to use a sedimentation tank. This kind of biofilm system can be used to a considerable extent for treating wastewater residues where simultaneous nitrification and denitrification (SND) can take place [6]. The SND reaction is much more advantageous when compared with the traditional method of nitrogen removal [7] because it can conserve energy sources, organic carbon, and alkalinity, shorten the reaction time, and curtail the production of sludge [8], [9]. Periodic backwashing in BAFs is necessary to avoid blockage of the system due to the entrapment of solids and biofilm growth. BCAs are much more advantageous in enhancing the original PFC, as they have the unique capability of achieving nutrient removal in a single reactor without requiring additional sedimentation [4].

In the present study, a BCAs biofilm pilot test was studied under various operating conditions for wastewater with varying secondary effluents. The purpose was to investigate the effect of BCAs biofilm on the removal of organic matter and ammonia and to provide the parameters in lieu of the PFC, especially to meet national limits of ammonia and benzene substances in the air of a workshop.

2. MATERIALS AND METHODS

2.1. REACTOR SETUP

The devices were designed according to the PFC characteristics so that the PFC was enhanced effectively after the success of the experiment. The pilot-scale test process is shown in Fig. 1. The influent wastewater was pumped to the bottom of a $\Phi 1.5 \text{ m} \times 3.5 \text{ m}$ cylinder and wastewater with aerated air raised together in a compatible manner. The depth of the packing media was 1.5 m, the distance between the me-

dia and the outlet of the treatment device was 0.5 m, and the distance from the media to the bottom of cylinder was 1.5 m. The density of the packing media was 14 kg/m^3 with the specific surface area of $1538.0 \text{ m}^2/\text{m}^3$. The diameter of the plastic wreath was 8.0 cm and the distance between adjacent spacers was 2.6 cm with the fibre length of 6.0–7.0 cm.

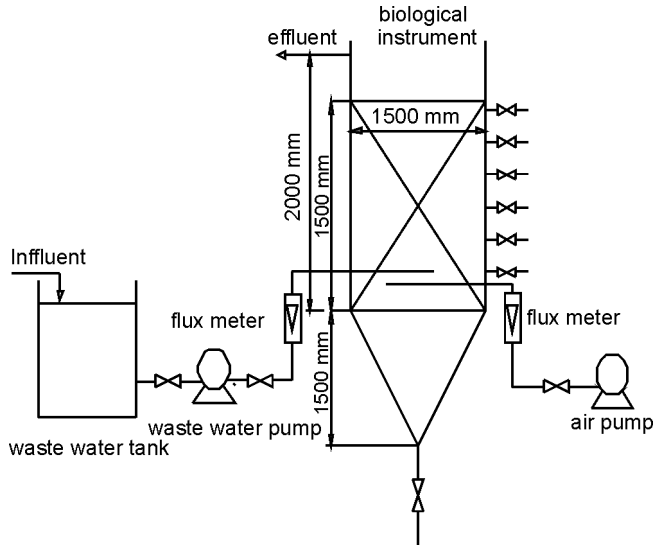


Fig. 1. The pilot-scale test stand

The rope-type of media is shown in Fig. 2. A combined support frame was affixed in the cylinder for supporting the fibres. Air was supplied to the reactor through four air screen diffusers located at height of 1.5 m from the reactor base. A valve connected to the air supply line was used to initiate and cut off the air supply and an airflow meter was used to control the aeration. A peristaltic pump, valve, and water flow meter were used to control the wastewater flux. The dissolved oxygen and a pH probe were used for continuous monitoring.

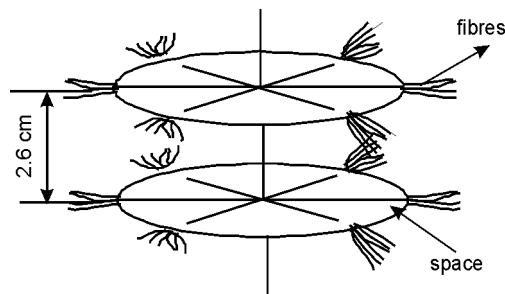


Fig. 2. The rope-type of media used in this study

2.2. THE INFLUENT CHARACTERISTICS AND OPERATION

After a run-in-period, the pilot scale test was conducted with respect to the secondary effluent of the A/O process. The results showed that the BCAs processes for wastewater were practical in terms of technique. The characteristics of the experimental influent are given in Table 1.

Table 1

Main characteristics of the experimental influent

Parameter	Influent	Effluent standard
COD _{Cr} , mg/dm ³	67.49–147.00	100
BOD ₅ , mg/dm ³	6.95–23.52	20
NH ₃ -N, mg/dm ³	6.34–39.36	15
SS, mg/dm ³	46.80–63.00	70
NO _x -N, mg/dm ³	14.62–22.52	–
pH	6.1–7.5	6.0–9.0
Alkalinity, mg/dm ³	0.00–1.50	–

2.3. ANALYTICAL METHODS

Most routine items of chemical analysis, such as COD_{Cr}, BOD₅, SS, NH₃-N, and alkalinity, were conducted according to the standard of APHA [10].

3. RESULTS AND DISCUSSION

3.1. BIOLOGICAL FILM IN ACCLIMATION

Firstly, untreated chemical wastewaters, then activated sludge were introduced to the experimental devices at the concentration of 2 g/dm³. The biological film with the dust colour could form gradually after five days of aeration. Secondly, untreated chemical wastewater was continuously introduced to the test devices under influent flux of 0.5 m³/h and optimum ratio of 2.66:1 for the air to wastewater, until the removal efficiency of COD_{Cr} and NH₃-N reached 70% and 50%, respectively. The third step, the input of effluent wastewater from the A/O process was combined at the same ratio of air to wastewater until the removal efficiency of COD_{Cr} and NH₃-N reached 20% and 10%, respectively. Finally, the biological film was developed successfully under acclimation.

3.2. INFLUENCE OF THE VOLUMETRIC LOADING RATE ON COD_{Cr} AND THE REMOVAL EFFICIENCY

The experimental relationships between the influent flux, hydraulic retention time (HRT), and hydraulic loading rate (HLR) under the optimum ratio of the air to wastewater flux of 2.66:1 is summarized in Table 2. The volumetric loading rate (VLR) of COD_{Cr} and the removal efficiency are shown in Fig. 3.

Table 2

Experimental relationships between
the influent flux, HRT, and HLR

Influent flux, m^3/h	0.3	0.4	0.5	0.6	0.75	1.00	1.25	1.50
HRT, h	10.0	7.5	6.0	5.0	4.0	3.0	2.4	2.0
HLR, $m^3/(m^2 \cdot h)$	0.170	0.226	0.283	0.339	0.425	0.566	0.707	0.849

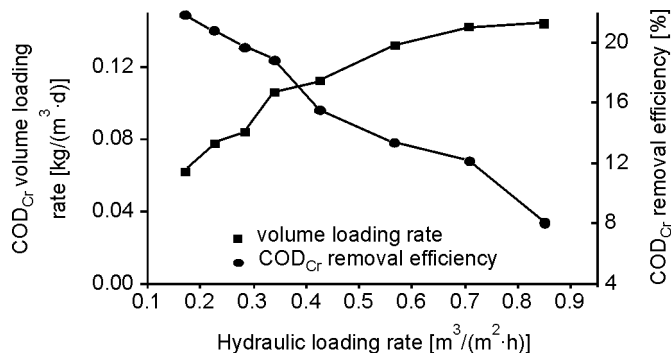


Fig. 3. Dependences of the volume loading rate and removal efficiency of COD_{Cr} on the hydraulic loading rate

As the HLR increased, the COD_{Cr} VLR increased from $0.062 \text{ kg}/(m^3 \cdot d)$ to $0.144 \text{ kg}/(m^3 \cdot d)$ and the COD_{Cr} removal efficiency decreased. The HRT increased when either the HLR or the wastewater velocity decreased, so that higher removal efficiency for COD_{Cr} was obtained while the VLR was at a lower level. Since the HRT of the PFC was 4 h, $0.425 \text{ m}^3/(m^2 \cdot h)$ was preferred as the HLR for reforming the PFC (Table 2, Fig. 3).

The influence of the VLR and the removal efficiency for COD_{Cr} on the influent organic concentration are shown in Fig. 4. The COD_{Cr} VLR increased with the COD_{Cr} concentration, it increased from the initial value of $0.062 \text{ kg}/(m^2 \cdot d)$ to $0.214 \text{ kg}/(m^2 \cdot d)$ because the COD_{Cr} concentration show a linear correlation with the BOD_5 concentration; further, higher the removal of BOD_5 , higher the VLR and removal efficiency of COD_{Cr} were obtained. When the BOD_5 effluent concentration decreased from

23.52 mg/dm³ to 6.00 mg/dm³, the COD_{Cr} effluent concentration decreased from 132.70 mg/dm³ to 100.24 mg/dm³ and the COD_{Cr} removal efficiency was 24.46%, respectively (Fig. 4).

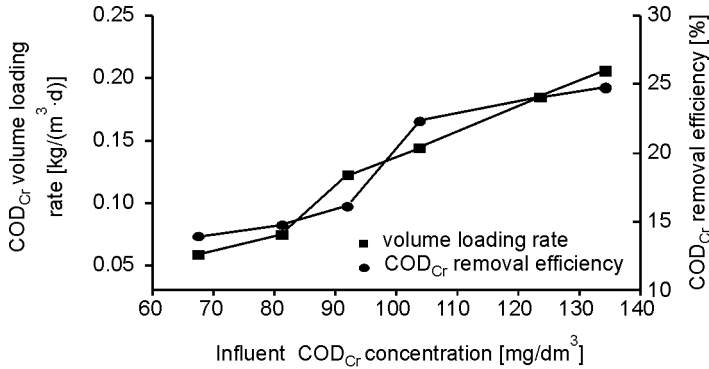


Fig. 4. Dependences of the volume loading rate and removal efficiency of COD_{Cr} on the influent organic concentration

The SS VLR and removal efficiency are shown in Fig. 5. The HLR did not influence the SS removal efficiency but the concentration of the principal SS removal depends on deposition. The concentration of the effluent SS was 16.50–26.33 mg/dm³, and the SS removal efficiency was 50.43–56.54%.

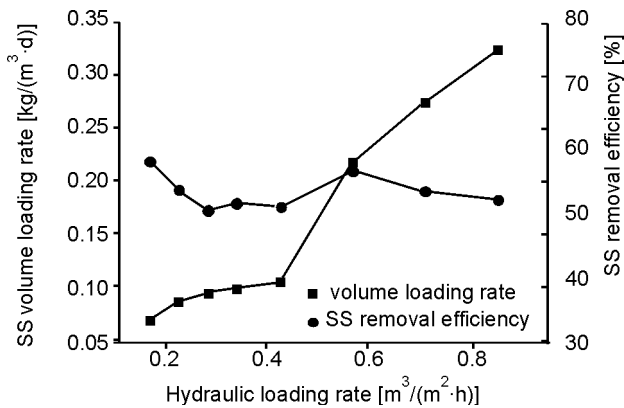


Fig. 5. Dependences of the SS volume loading rate and removal efficiency on the hydraulic loading rate

Relationship between the concentration of the influent SS and the corresponding COD_{Cr} was studied by determining the decrease of the COD_{Cr} concentration in relation to the increase of the SS concentration after the wastewater was allowed to settle for 4 h at room temperature. Such relationship is shown in Fig. 6. The SS concentration

decreased and the removal efficiency increased with the increase of COD_{Cr} VLR. The COD_{Cr} concentration decreased to the range of 14.01–20.99 mg/dm^3 , while the corre-

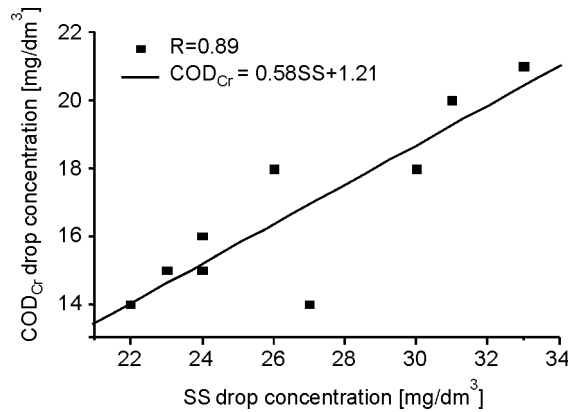


Fig. 6. Dependence of the COD_{Cr} concentration on the influent SS concentration

sponding SS concentration decreased in the range of 22.08–32.95 mg/dm^3 . SS concentration of 1 mg/dm^3 yielded the COD_{Cr} concentration of 0.58 mg/dm^3 which was different from the estimated COD_{Cr} concentration of 1.42 mg/dm^3 [11].

3.3. INFLUENCE OF THE VLR OF $\text{NH}_3\text{-N}$ AND THE REMOVAL EFFICIENCY

The VLR and removal efficiency of $\text{NH}_3\text{-N}$ are shown in Fig. 7. While the $\text{NH}_3\text{-N}$ VLR increased from 0.011 $\text{kg}/(\text{m}^3 \cdot \text{d})$ to 0.016 $\text{kg}/(\text{m}^3 \cdot \text{d})$, the $\text{NH}_3\text{-N}$ VLR did not change much more comparing to the change of the HLR. The $\text{NH}_3\text{-N}$ VLR was

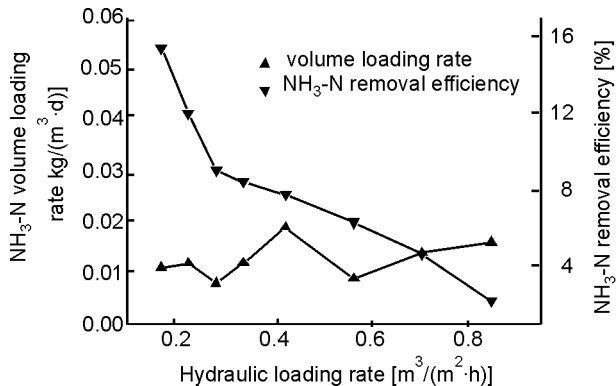


Fig. 7. Dependences of the $\text{NH}_3\text{-N}$ volume loading rate and removal efficiency on the hydraulic loading rate

changed more as the influent alkalinity (Table 3) is changed, and the $\text{NH}_3\text{-N}$ removal efficiency decreased as the HLR increased. When the HLR is $0.425 \text{ m}^3/(\text{m}^2\cdot\text{h})$, the $\text{NH}_3\text{-N}$ removal efficiency was 7.75% and the effluent concentration was $18.62 \text{ mg}/\text{dm}^3$ respectively, the $\text{NH}_3\text{-N}$ VLR was subject to the limit of the reactive condition and was basically unchanged with the HLR. The wastewater velocity and/or HLR increased as the HRT decreased; hence, the $\text{NH}_3\text{-N}$ removal efficiency was in the lower range because the pollutants were not totally degraded and had already left the reactor [12].

Table 3

Relationships between the influent alkalinity consumed, $\text{NH}_3\text{-N}$ removal, and increased in $\text{NO}_x\text{-N}$

ΔTB [mmol/dm ³]	$\Delta\text{NH}_3\text{-N}$ [mg/dm ³]	$\Delta\text{NO}_x\text{-N}$ [mg/dm ³]	$\Delta\text{TB}/\Delta\text{NH}_3\text{-N}$	$\Delta\text{NO}_x\text{-N}/\Delta\text{NH}_3\text{-N}$
0.00	0.00–1.12	1.07–2.04	0	0.95–1.82
0.06	0.00–1.12	1.68–2.58	0.00–0.05	1.50–2.33
0.10	1.12–2.24	2.07–2.68	0.05–0.09	0.54–1.19
0.20	2.12–3.43	2.97–3.09	0.06–0.09	0.90–1.40
0.28	2.68–3.87	3.51–3.67	0.07–0.10	0.95–1.31
0.70	7.85–11.21	5.9–12.24	0.06–0.09	0.75–1.09
0.90	13.45–14.57	9.41–12.63	0.06–0.07	0.70–1.06
1.08	15.65–18.69	11.11–16.57	0.06–0.07	0.71–1.06

Higher the alkalinity in normal nitrification processes, more $\text{NH}_3\text{-N}$ substances is removed and the $\text{NO}_x\text{-N}$ substances produced. Thus, the alkalinity concentration of $0.143 \text{ mmol}/\text{dm}^3$ would be consumed and $\text{NO}_x\text{-N}$ concentration of $1 \text{ mg}/\text{dm}^3$ would be produced for the theoretical removal of $\text{NH}_3\text{-N}$ of $1 \text{ mg}/\text{dm}^3$ [13]. The residual alkalinity of the influent was $0\text{--}1.50 \text{ mmol}/\text{dm}^3$. The relationships between the influent alkalinity consumed, $\text{NH}_3\text{-N}$ removal, and increase of $\text{NO}_x\text{-N}$ are given in Table 3. From Table 3, the ratio of $\Delta\text{TB}/\Delta\text{NH}_3\text{-N}$ is $0.05\text{--}0.10 \text{ mmol}/\text{mg}$ (less than the theoretical value of $0.143 \text{ mmol}/\text{mg}$) and the ratio of $(\Delta\text{NO}_x\text{-N})/(\Delta\text{NH}_3\text{-N})$ is $0.54\text{--}2.33$.

The results show that parts of $\text{NH}_3\text{-N}$ were used to form microbiological cells in function of assimilation, while the alkalinity concentration consumed was lower than $0.10 \text{ mmol}/\text{dm}^3$. Parts of $\text{NH}_3\text{-N}$ were consumed as a part of the main function of nitrification when the alkalinity concentration consumed was higher than $0.10 \text{ mmol}/\text{dm}^3$ and lower than $0.70 \text{ mmol}/\text{dm}^3$. When the alkalinity concentration consumed was higher than $0.70 \text{ mmol}/\text{dm}^3$ or even when the concentration was lower than 1.08, the ratio of $(\Delta\text{NO}_x\text{-N})/(\Delta\text{NH}_3\text{-N})$ was $0.70\text{--}1.09$. The results were applied to Yaman's data [14]. The discrepancy was due to SND [15]. It was found that a sufficient alkalinity in the system was critical for nitrifying the ammonium wastewater.

3.4. INFLUENCE OF COD_{Cr} AND NH₃-N REMOVAL ON THE STUFFING HEIGHT

The quantities of COD_{Cr} and NH₃-N removed varied with the stuffing height. The optimum stuffing height was measured for the best quantities of removal of COD_{Cr} and NH₃-N at lower ratio of C/N of 4.4. The dependence of COD_{Cr} and NH₃-N removal on various stuffing heights is shown in Fig. 8.

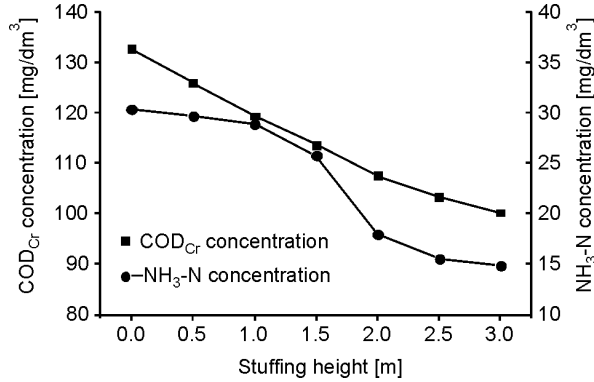


Fig. 8. Dependences of the COD_{Cr} and NH₃-N removal on the stuffing height

At the distance of 1 m from the bottom of the reactor, the removal of the COD_{Cr} concentration increased to 10.02%, while the removal of the NH₃-N concentration increased to only 5.14%. These shows that bacterial carbonaceous oxidation was more active than bacterial nitrification below the stuffing height of 1m when the wastewater just entered the instrument. The removal of NH₃-N concentration was 15.37% at the height of 1.5 m, thus, the nitrifying bacteria began to work well once the concentration of degradable carbon reached a lower level. The filler height of 3 m could meet demands for treating the wastewater (Fig. 8).

The best-fit mathematical model for COD_{Cr} removal was obtained for the related parameters from Figs. 4 and 8 for yielding the best representation of Jinbao's design [16]. An empirical depth parameter equation for NH₃-N removal was found for application to the Gujer–Boller model [11]. Two appropriate mathematical models represent Eqs. (1) and (2). The results show that a suitable HLR and a suitable height of the reactor were necessary to achieve the effective removal of both COD_{Cr} and nitrogen

$$\ln \frac{\rho_{so}}{\rho_s} = K (\rho_{so})^m \left(\frac{q_v}{A} \right)^n h \quad (1)$$

$$\frac{Haj_{N,max}}{\frac{q_v}{A}} = \rho_{sno} - \rho_{sne} + M \ln \frac{\rho_{sno}}{\rho_{sne}} \quad (2)$$

The issues and performance parameters regarding Eqs. (1) and (2) are presented in Table 4.

Table 4

Summary of the fit performance parameters

Parameter	Value
Influent COD _{Cr} concentration, ρ_{so}	132.70 mg/dm ³
Range of the effluent COD _{Cr} (over various heights), ρ_s	126.10–100.24 mg/dm ³
Constant concerning the influent concentration, m	1.065
Constant concerning the hydraulic loading rate, n	-0.490
Hydraulic loading rate, q_v/A	0.425 m ³ /(m ² ·h)
Range of the height of the reactor, h	0.0–3.0 m
Constants concerning influent concentration and hydraulic loading rate at 20 °C, K	0.000337
Height of the reactor, H	3.0 m
Specific surface area of the stuffing, a	1538 m ² /m ³
Maximum specific rate of removal of NH ₃ -N, $j_{N,max}$	0.0015 g/(m ² ·h)
Influent NH ₃ -N concentration, ρ_{sno}	30.44 mg/dm ³
Effluent NH ₃ -N concentration, ρ_{sne}	30.44–14.79 mg/dm ³
Half-saturation NH ₃ -N coefficient, N	0.8729 mg/dm ³

3.5. APPLICATION OF THE EFFECT OF TREATED WASTEWATER

Through technological improvements and actual operating results of several years, the treated wastewater of reuse by BCAs can meet the needs of sludge dewatering belts. The influence of filtrated water for sludge dewatering belts with the groundwater and reused wastewater, and the influence of the air of a workshop for the groundwater and reused wastewater are shown in table 5 and table 6, respectively. In the reuse of tertiary wastewater, while reducing the costs of wastewater treatment of sludge dewatering belts, annual costs with flocculant dosing can reduce 200 000 yuan RMB per pool

Table 5

Influence of filtrated wastewater on groundwater and reused wastewater

Item	COD _{Cr} [mg/dm ³]		SS [mg/dm ³]	
	Groundwater	Wastewater	Groundwater	Wastewater
1	2829.57	1562.91	1283	894
2	1020.27	1377.48	339	585
3	1160.89	1422.10	986	649
4	1235.19	1736.86	754	1071
5	1267.58	1247.68	1025	1062
Average	1249.18	1469.41	877.4	852.2

Table 6

Influence of air of workshop on groundwater and reused wastewater

Item	Groundwater [mg/m ³]	Wastewater [mg/m ³]	National standards [mg/m ³]
Benzene	0.58	0.68	5
Ammonia	0.95	1.15	30
Aniline	0.22	0.27	5
Toluene	0.41	0.21	5
Nitrobenzene	0.19	0.32	1
Styrene	0.23	0.28	40
Xylene	0.41	0.53	100

and the groundwater of 876 000 t cannot be consumed each year, the annual cost of 360 000 yuan RMB can be saved each year.

4. CONCLUSIONS

A biofilm pilot test in a biological contact aerator was studied for complex chemical secondary effluent wastewater with biochemical characteristics and various operational conditions in lieu of the PFC.

The effluent COD_{Cr} could decreased from 132.70 mg/dm³ to 100.24 mg/dm³ and the NH₃-N could declined from 30.44 mg/dm³ to 14.79 mg/dm³ through the BCAs under a lower ratio of C/N of 4.4. The SS concentration of 1 mg/dm³ yielded a COD_{Cr} concentration of 0.58 mg/dm³. The ratio of (Δ NO_x-N)/(Δ NH₃-N) was 0.7 and the discrepancy was due to SND. The removal efficiency through the BCAs for COD_{Cr} and NH₃-N was 24.46% and 51.41% respectively, under HLR of 0.425 m³/(m²·h). Since two appropriate mathematical models and parameters were obtained for achieving the effective removal of both COD_{Cr} and nitrogen, the effluent quality can satisfy national discharged limits and the requirements of washing belts, particularly to meet national limits of ammonia and benzene substances, etc. in the air of a workshop.

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LUCJAN PAWŁOWSKI*

EFFECT OF MERCURY AND LEAD ON THE TOTAL ENVIRONMENT

Mercury and lead are widely used in nowadays economy. However, by using these toxic metals, we disperse them around the planet, pollute it and, since they are not biodegradable, threaten future generation with unsafe environment. The other side of the problem is that they are nonrenewable resources and therefore current estimates suggest that, at present levels of consumption, there is enough lead for 58 years and mercury for 46 years, to mention just a few of the best known heavy metals. A role of these metals in the total environment is discussed in the paper.

1. INTRODUCTION

The concept of sustainable development was introduced in Burtland's famous report *Our Common Future*, which generally says that sustainable development is that which meets the needs of the present without threatening the abilities of future generations to meet their needs.

Talking about sustainable development on the ground of moral values, one can speak of inter- and intra-generational justice. Inter-generational justice refers to the demands of future generations that resources and the quality of the environment be left in a state that allows them to live [1]. Intra-generational justice (i.e. justice within a generation) refers to the present generation and demands equal access to available resources. Both of these principles must be borne in mind when discussing sustainable development.

Practical implementation of these principles is complicated because of many dimensions: philosophical, social, ecological, economical and technical [2]. In this discussion, let us focus on defining the duties arising from the implementation of sustainable development. That means the transition to defined duties on the basis of ethics, where we can talk about the need to ensure inter- and intra-generational justice [3, 4].

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Initially heavy metals are used as new materials for the production of goods. Since they are non-renewable resources and their amounts are limited on our planet, sooner or later they may be exhausted, and thus future generations may not be able to meet their needs for heavy metals. This is one side of the problem. The other is that by the use of heavy metals by our civilization, they do not disappear from the planet, but are dispersed throughout Earth's surface, polluting it, and thus threatening a safe environment for future generations.

The present world is developing unsustainably. There has been enormous technological progress; however, our technical abilities to change the world are so powerful that they may even lead to its destruction [4, 5]. The almost geometric progress of our technical abilities to change the world has left the development of social sciences far behind, and does not allow answering the question of what values such changes serve. The fact that resources are becoming less available makes it all the more serious [6, 7].

A lot has been said and written in recent years about climate change, and much less about the fact that the main fossil fuels and non-renewable resources may be exhausted. The consequences to the world of energy and non-renewable resource shortages could be much more severe than the greenhouse effect [8].

Current estimates are that, at the present levels of consumption, there is enough oil for about 40–50 years, natural gas for about 60–70 years and coal for ca. 140–150 years. The situation is no better for metals. At the present level of consumption, there is enough copper for about 66 years, zinc for 23, lead for 58, mercury for 46, and cadmium for ca. 31 years, to mention just a few of the best-known heavy metals [9]. This does not mean that after that time heavy metals would cease to be available; their shortage would cause poorer deposits to be exploited and substitutes to be more widely used. Nevertheless, the resources of heavy metals are not infinite, and sooner or later they may be exhausted. The sustainable approach requires the slowing of use of heavy metals by saving, recycling and substitution by more available materials, and as well preventing their dispersion throughout the environment.

Even if we assume a large error in the estimates, one must accept that a major crisis in access to conventional resources will occur within a short time, measured rather in decades than in centuries. This means that one of the cardinal rules of sustainable development, namely inter-generational justice, is at stake. The present generation seems to be living at the expense of future generations [10].

All the above clearly indicates that the development of modern civilization is highly unsustainable [11], and seems to show that full sustainability is impossible; however, this does not mean that we can do nothing. From a practical standpoint, the goal of sustainability should be to minimize, as far as practical, the use of energy and irreplaceable raw materials. We should also seek to develop sources of energy and materials which are replaceable or self-regenerating, and as non-polluting as practically possible [12–14].

2. PROBLEMS WITH HEAVY METALS

Mercury and lead are the best-known heavy metals and have been used by mankind since ancient times. They belong to a limited class of elements that can be described as purely toxic, and are still widely used and important to our economy. However, because they are toxic, persistent and bioaccumulative pollutants continuously dispersing through the whole surface of the earth, they pose a serious threat to the global environment.

Since heavy metals are elements, they cannot be broken down and therefore thus persist in the environment. Unlike many organic pollutants, which eventually degrade to carbon dioxide (CO₂) and water, heavy metals tend to accumulate in the environment, especially in lake, estuarine or marine sediments. Metals can be transported from one environmental compartment to another. Many heavy metals are toxic to organisms at low concentrations; however, some such as copper and zinc are also essential elements. Concentrations of essential elements in organisms are normally homeostatically controlled, with uptake from the environment regulated according to nutritional demand. Effects on the organisms are manifested when this regulation mechanism breaks down as a result of either insufficient (deficiency) or excess (toxicity) metal. Mercury and lead, however, have adverse effects even at exposure to low concentrations.

2.1. MERCURY

The oldest information on the use of mercury is from China. The ancient Chinese believed that mercury had a positive effect on health and could prolong life. One of China's emperors, Qin Shi Huang Di, drank mercury because he believed that it gave him eternal life. The ancient Egyptians and the Romans used mercury in cosmetics, and alchemists thought mercury was the first matter from which all metals were formed.

Nowadays, mercury is one of the most widely used heavy metals in industry (Table 1). More significant, however, is its anthropogenic emission in the environment. According to Pacyna et al. [16] and Streets et al. [17], total mercury emissions from anthropogenic sources were 2 320 Mg (Table 2) – calculated from estimated of emission factors (Table 3).

The greatest mercury emissions are from coal and oil combustion (810 Mg/yr) and gold mining (400 Mg/yr). Mercury emissions from natural sources (Table 4) are much higher (5207 Mg/yr) than from anthropogenic sources (2320 Mg/yr). The higher emission from natural sources is caused by the circulation of mercury in the environment. Due to oxidation-reduction and microbial processes, mercury is volatilized mostly to the atmosphere and redeposited back on the surface of the Earth, then emitted again to the atmosphere due to the above mentioned processes. The flux of mercury from natu-

ral sources is therefore much higher than that from anthropogenic origins. The circulation of mercury in the environment is responsible for the growing contamination of the whole surface of our planet. The levels of atmospheric mercury are increasing in the remote troposphere, far from known sources [20].

There are two main types of reaction in the mercury cycle that convert mercury into its various forms: oxidation-reduction and methylation-demethylation. In oxidation-reduction reactions, mercury is either oxidized to a higher valence state (e.g., from the relatively inert Hg^0 to the more reactive Hg^{2+}) or through the loss of electrons reduced, the reverse of being oxidized, to a lower valence state.

Table 1

Mercury consumed [Mg] in 2000 [15]

Item	European Union	United States	Rest of world	Totals
Hg consumed in batteries	15	16	1050	1081
Hg consumed in dental amalgams	70	44	158	272
Hg consumed in lighting	21	17	53	91
Hg consumed in electrical control and switching	25	50	79	154
Hg consumed in other products and processes	50	50	75	175
Hg consumed in measuring and control devices	26	35	105	166

Table 2

Global mercury emission from anthropogenic sources, data for 2008

Source category	Hg emission [Mg/yr]	Reference
Coal and oil combustion	810	[18]
Non-ferrous metal production	310	
Pig iron and steel production	43	
Cement production	236	
Caustic soda production	163	
Mercury production	50	
Artisanal gold mining production	400	[19]
Waste disposal	187	[18]
Coal bed fires	32	
VCM production	24	
Others	65	
Total	2320	

Another problem with pollution with mercury is an indoor environment, since this is where an average person spends most of their life. When spilled in a small, poorly-ventilated room, mercury can pose significant health threats. Very small amounts of

metallic mercury, released into an enclosed space, can raise air concentrations to levels harmful to health. In addition, metallic mercury and its vapours are extremely difficult to remove from clothes, furniture, carpets and other porous items.

Table 3

Emission factors adopted to estimate anthropogenic emissions [16]

Source category	Unit	Emission factor
Coal combustion power plants	g·Mg ⁻¹	0.04–0.3
Coal combustion in residential and commercial boilers		0.1–0.5
Oil combustion		0.058
Biofuel combustion		0.02
Cu smelting		5.0–6.0
Pb smelting		3.0
Zu smelting		7.5–8.0
Cement production		0.065–0.1
Pig iron and steel production		0.04
Municipal wastes incineration		1.0
Sewage sludge wastes		5.0
Mercury production (primary)		kg·Mg ⁻¹
Gold production (large scale)	g·g ⁻¹	0.5

Table 4

Global mercury emissions by natural sources estimated for 2008 [18]

Source	Emission [Mg·yr ⁻¹]	Contribution [%]
Oceans	2682	52
Lakes	96	2
Forests	342	7
Tundra/grassland/savannah/prairie/chaparral	448	9
Desert/metalliferous/non-vegetated zones	546	10
Agricultural areas	128	2
Evasion after mercury depletion events	200	4
Biomass burning	675	13
Volcanoes and geothermal areas	90	2
Total	5207	100

As mentioned above, implementation of sustainable development requires a reduction in energy consumption because natural reserves are limited and their combustion increases the concentration of CO₂ in the atmosphere, which seems to lead to climate change [7]. One proposed method of reducing energy consumption is to use fluorescent bulbs. However, the solution to one global problem creates another – fluorescent bulbs contain a small amounts of mercury vapour and a larger amounts of mercury in

a powder or dust form, both of which can become airborne if the bulb breaks. If the breakage is not cleaned up properly, the mercury may continue to circulate. Disposing of these bulbs in the trash can cause also serious harm to health and the environment.

The US Environmental Protection Agency sets a reference concentration of $0.3 \mu\text{g Hg}/\text{m}^3$ for inhalation exposure to mercury. The reference concentration is a screening tool to help risk assessors to determine where to focus their investigation into hazardous exposures – adverse health effects do not necessarily result from exposure at that concentration. For example, if $0.3 \mu\text{g Hg}/\text{m}^3$ was measured in an air inside a building, the EPA would further investigate the exposure.

Similarly, the US Agency for Toxic Substances and Disease Registry (ATSDR) has set a minimal risk level (MRL) for inhalation exposure for mercury at $0.2 \mu\text{g Hg}/\text{m}^3$. The MRL is an estimate of the daily human exposure to a hazardous substance that is likely to be without appreciable risk of adverse health effect over a specified period of time. ATSDR also recommends an action level of $1.0 \mu\text{g Hg}/\text{m}^3$ for remediation if exceeded in indoor air.

Table 5

Projected global mercury use in 2020 [15]

Use category	Global demand 2000 [Mg]	Prospects for mercury demand to 2020	Projected global demand 2020 [Mg]
Chlor-alkali industry	797	significant decline over next 10–20 years	280
Small-scale gold/silver mining	650	unpredictable, but some decrease in the level of exploitation	400
Batteries	1081	steep decline	100
Dental amalgam	272	gentle decline	250
Measuring and control	166	general decline	100
Lighting	91	gradual increase, at least in the foreseeable future	120
Electrical control and switching	154	general decline	100
Other uses	175	variable, especially in cosmetics	150
Total demand	2286		1500

Control of mercury concentration in indoor environments seems to be very important due to mass use of fluorescent lamps in EU countries. One must consider that fluorescent bulbs contain 0.5–1000 mg Hg per bulb. This is only the source where use of mercury will increase in years to come (Table 5).

2.2. LEAD

Lead is another heavy metal with a global impact. It was one of the earliest metals discovered by man and was in use by 3000 BC. The ancient Romans used lead for

making water pipes and lining baths. They also used lead pots or lead-lined copper for boiling crushed grapes to make wine. According to the Roman winemaker Columella, lead improves the taste of wine. It was discovered later that, in lead pots, lead acetate with a sweet taste is formed. Lead touched many areas of Roman life. It was used in pipes, dishes, cosmetics, coins and paints. Some historians believe that many among the Roman aristocracy suffered from lead poisoning and that the fall of the Roman Empire was caused by the degeneration of the ruling class caused by lead poisoning. Even in the Middle Ages, lead acetate, called sugar of lead, was used to sweeten wine.

For centuries, lead compounds have provided pigments for paints, and are still widely used. The total consumption of lead continues to grow, from 7.297 mln Mg in 2004 to 8.649 mln Mg in 2009. One positive aspect, from the sustainability standpoint, is that a significant proportion of the lead used has been recycled (Table 6).

Table 6

Global lead production and consumption [mln Mg] [21]

Source	Year					
	2004	2005	2006	2007	2008	2009
Mine production	3.865	4.202	4.410	4.500	4.857	4.798
Recycling	3.130	3.422	3.525	3.626	3.896	4.029
Total production	7.005	7.624	7.935	8.126	8.653	8.827
Total consumption	7.297	7.786	8.063	8.182	8.649	8.756

In terms of tonnage consumption of lead since 1960, the battery market increased almost seven-fold while almost all the other sectors experienced real as well as proportional declines. The growth in total demand for lead has therefore been due almost exclusively to the demands of the battery market. Despite the decline in many of the non-battery uses of lead, some interesting prospects exist for new commercial-scale applications in the future. Significant among these is the use of lead for nuclear waste disposal. Because lead absorbs alpha and gamma rays it can be used as containers for nuclear wastes. As the demand for non-fossil-fuel energy sources intensifies, prospects for nuclear power – and hence for nuclear waste disposal – seem likely to grow. Liquid metal magnetohydrodynamics (LMMHD) is another energy-related potential use of lead. In LMMHD (currently only at the pilot stage), molten lead flows in an enclosed loop through an intense magnetic field to generate an electric current. The system can employ low-grade heat sources and would be particularly suitable for installation in remote locations. With a requirement of about 200 tonnes of lead per MW of installed power, could be an important new market for the metal. A third new use of lead which has already proven its effectiveness is in earthquake to stabilize buildings.

The present emissions of lead to the environment is declining like the emissions from burnt gasoline, where in 1960 nearly 200 000 Mg of lead was used, reaching

a peak of 300 000 Mg in the early 1970s and has declined steadily ever since. By 2005, consumption of lead as gasoline additives accounted for < 10 000 Mg. However, it is estimated that over the past five millennia about 300 million t of lead were released into the environment. Such consumption caused a global lead contamination of the whole environment due to circulation in soil, water and air. The amount of lead emitted to the environment over time is such that levels in the human body of today's population are 500–1000 times greater than that of their pre-industrial ancestors [22].

Low-level environmental exposure to lead is associated with multiple sources (petrol, industrial processes, paint, and solder in canned food, water pipes) and pathways (air, household dust, street dirt, soil, water and food). Evaluation of the relative contributions of sources is therefore complex and likely to differ between areas and population groups.

3. INTER- AND INTRA-GENERATIONAL JUSTICE

Referring to moral obligations drawn from the idea of sustainable development, one can distinguish two important terms: inter- and intra-generational justice.

3.1. INTER-GENERATIONAL JUSTICE

This is justice between the current generation and those that follow. The term was used in the Brundtland report definition of sustainable development.

Democracies – both the representative and the direct type – face a structural problem, namely the tendency to favour the present over the future. Future individuals are not yet born, and thus are unable to be involved in today's decision-making process.

Apart from an exhaustion of the source of heavy metals what may create a problem with manufacturing of some goods, the other problems for the future generation seems to be even more severe. All heavy metals when released to the environment remain there for an unlimited time, recycling among all compartments through the following mechanisms:

- Natural-source releases due to natural mobilization of naturally occurring heavy metals from Earth's crust such as by volcanic activity and weathering of rocks.
- Current anthropogenic (associated with human activity) releases from the mobilization of heavy metals impurities in raw materials such as fuels – particularly coal, and to a lesser extent gas and oil – and other extracted, treated and recycled minerals.
- Current anthropogenic releases of heavy metals used intentionally in products and processes, due to releases during manufacturing, leaks, disposal or incineration of spent products or other releases.
- Re-mobilization of historic anthropogenic heavy metals releases previously deposited in soil, sediments, water bodies, landfills and waste/tailings piles.

Global emissions remain high and, taking into account accumulation of metals in the environment, further emissions may threaten, above all, the health of children. For example nearly 1.7 million children aged 1–5 have blood levels of Pb \geq 100 μ g/L. Such a level will negatively affect their wellbeing.

Since the oceans are a sink for most heavy metals, there is a danger that growing heavy metal concentrations in the marine environment will disturb plankton growth. These may affect not only the food chain in the marine environment, but also decrease CO₂ assimilation by plankton, one of the very important global sinks of CO₂ – this would accelerate climate change.

A positive trend can also be observed. The anthropogenic emissions of lead in 32 EEA (European Economic Area) countries have declined by 88% during 1990–2007. This is primarily due to reductions in the road transport sector. The promotion of unleaded petrol within the EU through a combination of fiscal and regulatory measures has been a particular success story. EU member states and other EEA member countries have now phased out the use of leaded petrol, a goal regulated in the EU by the Directive on the Quality of Petrol and Diesel Fuels (98/70/EC). In 2007, the largest emitters of lead were Poland (responsible for 20% of total EEA-32 emissions), Spain (10%), Italy (10%) and Bulgaria (9%). All countries report lower emissions of lead in 2007 compared with 1990, with the only exceptions being Malta and Bulgaria [23].

Global change related to climate change and the role of CO₂ emissions has attracted worldwide attention [8, 24]. Not many know, however, that heavy metals can disturb the equilibrium of the global environment. In the extreme case of an excessive increase in their concentrations in the oceans, which are the sink for heavy metals, they may inhibit plankton growth. This would disturb the food chain in the oceans and in consequence decrease fish production to a catastrophic level. Plankton also plays an important role in the absorption of CO₂ from the atmosphere – one of the major sinks for CO₂. The disappearance of plankton from oceans would cause a catastrophic growth in the concentration of CO₂ in the atmosphere. Therefore, control of heavy metal emissions is of great global importance.

The improper control of heavy metals can lead to a substantial threat to the inter-generational justice – one of the fundamental principles of sustainable development. Therefore, studies of pathways of heavy metals in the environment are equally important as studies on greenhouse gases, as they may affect future life on our globe even more severely than greenhouse gas emissions.

In reference to the term ‘humanity ecological footprint’, which sets the smallest necessary area of the Earth’s surface for the human population to survive [25], it has been shown [26] that our planet’s capacity to sustain our population was exceeded in approximately 1986 (Fig. 1). Thus, the space available on our planet to sustain a decent life for the human population is already overloaded. There is no room for a growing population.

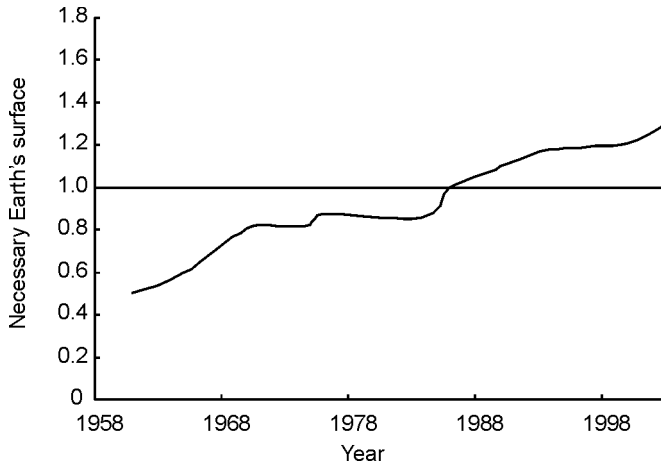


Fig. Global footprint for the period of 1958–1998.

3.2. INTRA-GENERATIONAL JUSTICE

Moreover, a second rule of sustainable development, intra-generational justice, is not respected either. The present course of development in our civilization makes it worse. With the fall of socialism, liberal capitalism, with its chief paradigm ‘grow-or-die’ became the leading socio-economic system [27]. As a consequence, the consumption of all environmental components increased, including non-renewable resources. This phenomenon was accompanied by a global concentration of economic power, associated by numerous ties with political influence [28].

Appealing to ruthless competition, with no regard to cooperation, has a disintegrating influence on social bonds and creates an atmosphere that favors struggle for dominance, especially economic, associated with political power [27]. In consequence we have economic and political elite with strong internal bonds, alienated from the rest of society, to an extent that ordinary people have little or no influence on social and economic processes. The criminal war in Iraq provides an example: had the decision to start the war been dependent on a referendum and not made in the privacy of cabinets of the economic and political elite, the war would never have begun.

As Hart [29] indicates, in 1960 the wealthiest 20% of the population owned 30 times as much wealth as the poorest 20%, whereas this ratio in 1991 reached 60 times, and 78 times in 2004. A UNDP report [30] provides information showing that the annual income of the 500 richest people in the world is equal to that of the 400 million most impoverished; Kofi Annan, Secretary-General of the UN, stated that almost half the population has an income of < \$2 a day.

Young children are undergoing rapid development, their systems are not fully developed, and consequently they are more vulnerable than adults to the effects of heavy

metals, especially lead. Children from poor families are more exposed to heavy metals because they live in older houses where paints containing heavy metals (Pb and Cd) have been used. They also live mostly in the more populated areas where emissions of Pb from gasoline are higher.

A study in the USA [31] showed that, during 1976–1991, when lead was removed from gasoline, the prevalent blood lead level of $\geq 100 \mu\text{g}/\text{dm}^3$ for children aged 1–5 years declined from 85.0% to 5.5% for non-Hispanic white children, and from 97.7% to 20.6% for non-Hispanic black children. The major cause of this decline was the removal of lead from gasoline. Sociodemographic factors associated with higher lead levels in children of non-Hispanic black race were low income and living in older housing. It was concluded that programs for the prevention of lead poisoning should target high-risk persons, such as children living in old houses, belonging to minority groups, and living in families with low incomes.

The worst situation, however, is in developing countries like Africa. Gasoline sold in most African countries contains 0.5–0.8 g Pb/dm³. In urban and rural areas and near mining centres, average lead concentrations reach 0.5–3.0 $\mu\text{g}/\text{m}^3$ in the atmosphere and $>1000 \mu\text{g}/\text{g}$ in dust and soils. In addition to automotive and industrial sources, cottage industries and the burning of paper products, discarded rubber, battery casings and painted woods for cooking and heating represent additional hazards to individual households [32].

Although African children are particularly predisposed to environmental lead exposure, because of their lifestyle and socioecological factors, a true picture of childhood lead poisoning in the continent remains undefined. Recent prevalence studies show that $> 90\%$ of the children in urban and rural communities of the Cape Province, South Africa have blood lead levels $\geq 100 \mu\text{g}/\text{dm}^3$. Studies in other countries likewise suggest that childhood lead poisoning is a widespread urban health problem throughout the continent [32].

4. CONCLUSION

Heavy metals, mainly mercury, lead and cadmium, are a global problem that needs to be addressed from a global and sustainable perspective, like climate change. Therefore, it was suggested the EU established a research project on the effects of heavy metals on the global environment. The research should concentrate on the following:

A better understanding of what happens to heavy metals from extraction through processing and manufacturing to their ultimate disposal.

Heavy metals have accumulated over the centuries in all parts of the environment and their fate and pathways within ecosystems need to be better understood.

The role of methylated heavy metals (monomethyl and dimethyl mercury; dimethyl, trimethyl and tetramethyl lead; and monomethyl cadmium) in the migration of heavy metals in the global environment needs to be better understood.

The role of heavy metals in the ocean biota needs to be better understood.

There is a need to develop a detailed global emissions inventory for mercury, lead and cadmium from anthropogenic sources for inclusion in the global tracer transport model.

There is a need to develop parameterizations for the exchange of mercury, lead and cadmium between the oceans, land surface and biosphere for inclusion in the global tracer transport model.

No doubt heavy metals are equally important from sustainable development and global perspective as the greenhouse effect, and an increase in the content of heavy metal in the global environment is more dangerous than increase in the content of greenhouse gases.

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STATISTICAL APPROACH TO ASSESSING GROUNDWATER POLLUTION FROM GASWORKS

The primary objective of this work was to ascertain the effectiveness of the Microtox system in assessing the quality of groundwater polluted with by-products of coal pyrolysis. Another major objective was to investigate how biological treatment contributes to the change in water toxicity. Making use of the results of toxicological and instrumental analyses, as well as of statistical methods, attempts were also made to specify which particular compound is the main contributing factor in the toxicity of water. When used for assessing the progress of the treatment process, the Microtox test proved very useful for application in the treatment of groundwater polluted by gasworks. The results obtained with this test have provided a reliable description of the course of the technological process, which can be efficiently corrected owing to a quick availability of the results of toxicological analysis. Another benefit offered by the Microtox test is that the use of statistical methods makes it possible to decide which of the compounds being components of the mixture is responsible for the toxicity of an environmental sample.

1. INTRODUCTION

The pollution of an aquatic environment derives from a wide diversity of polluting species, whose composition differs noticeably both in quantitative and qualitative terms. Those differences, as well as the interactions among the pollutants, make it difficult to assess explicitly the imminent threats and potential implications. A key issue is the choice of adequate analytical methods in order to detect and quantify the polluting substances occurring in the environment [1–4]. Analytical techniques for the control of chemical pollutants are costly, time-consuming, and in most instances apply to laboratory tests only. The costs involved can be reduced, when the test is targeted at the quantitative determination of a known pollutant. But they may increase considerably in the case of quantitative and qualitative analyses of multicomponent samples. It is essential to note, however, that the characteristics in terms of the quantitative and

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qualitative compositions of the polluting species fails to adequately describe their threats to living organisms [5–7].

Unbiased information on the variety of threats to which the aquatic environment is exposed can only be obtained by toxicity tests. Among various methods enabling qualitative assessments, the set of Microtox tests using the luminescent bacteria *Vibrio fischeri* bioindicators deserves particular attention. In the electron transport system of these bacteria, luciferase catalyzes the oxidation of the reduced substrate (reduced flavin mononucleotide, riboflavin phosphate or flavin adenin dinucleotide) [8]. The luminescence that occurs during the process is recorded with a photometer [9]. Other substrates participating in the reaction are oxygen and long-chain aldehyde. Under normal conditions, the test bacteria utilize approximately 10% of their energy for luminescence; in the presence of substances exerting a negative effect on cell metabolism, they react quickly and a drop in luminescence occurs. The straightforward structure of the test permits examination of diverse environmental samples (water, wastewater, soil). With the Microtox test it is possible to quickly assess the toxicity of environmental samples and the progress of the treatment process. As yet, little information is available on the problem of how the results of instrumental analyses compare with those of toxicological analyses. Some of the experiments were carried out by McDonald et al. [10] and Ntziachristos et al. [11]). Having such information at hand would promote a wider use of toxicological methods, such as screening or supplementary analyses, in physicochemical studies.

The aim of this study was to ascertain the applicability of the Microtox test in assessing the quality of groundwater polluted by gasworks.

2. MATERIALS AND METHODS

The natural groundwater samples, containing by-products of coal pyrolysis, were used for the toxicity tests. The tests were performed using the Microtox (Strategic Diagnostics Inc., Newark, USA) system, with luminescent bacteria *Vibrio fischeri* as the bioindicator. Lyophilized bacteria can be stored at $-20\text{ }^{\circ}\text{C}$ for one year, but they may be used at any time upon suspension in deionized water. When placed in a diluent (2% NaCl), the bacteria emit light with a constant intensity for 1–1.5 h. The measure of toxicity is the decrease in luminescence after 15-min incubation of the test bacteria in the presence of the compound being examined. Tests were performed with an M 500 analyzer and lyophilized bacteria, according to the standard procedure specified by the manufacturer (SDI). The results were calculated using the manufacturer's software MicrotoxOmni. The results of analyses are expressed in toxicity units (TU) calculated in terms of EC_{50} (sample concentration reducing luminescence by 50%), which was determined for particular groundwater samples according to the formula $TU = 1/EC_{50} \times 100$.

Statistical analysis was carried out using Statgraphics packets; in regression analysis use was made of linear, exponential, reciprocal and multiplicative models [12].

3. RESULTS AND DISCUSSION

The polluted groundwater samples were subject to toxicological analyses before and after biological treatment (activated sludge process – pilot plant). The results revealed a direct influence of the treatment process on the toxicity of the sample. After treatment in the bioreactor, toxicity level was reduced noticeably as compared with raw groundwater samples (Tables 1, 2). However, the extent of reduction varied from one sample to another, and in most instances did not depend on the toxicity level of the raw sample. Thus, on 26.04.2010, after passage through the bioreactor, the toxicity of $TU = 400$ which was measured in the raw sample decreased to $TU = 47.6$, whereas one month later it decreased from $TU = 153.8$ to $TU = 66.7$. This should probably be attributed to some other physicochemical and biological factors which affected the treatment process at that time.

Table 1

Chemical contaminations of water recorded from 2009.11.23 to 2010.04.19 [mg/m^3]

Parameter	2009				2010				
	11.23	12.07	12.07	12.21	01.04	01.04	02.02	04.12	04.19
Measuring point	Raw water		Bioreactor	Raw water		Bioreactor		Raw water	
Toxicity [TU]	31.7	33.0	43.5	45.4	83.3	37.0	43.5	200	153.8
TOC	36.8	35.2	64.6	38.9	40.9	61.4	60.4	169	148
MAH	12 399	10 333	5006	10 868	11 379	7379.1	1912.8	20 304	10 191
Phenol	110	90	80	82	92	130	53	195	140
2-Methylphenol	180	190	150	160	170	23	22	2079	2500
3-Methylphenol	150	140	37	130	140	61	12	3000	3700
4-Methylphenol	240	240	38	210	230	23	57	5012	6700
2-Ethylphenol	140	140	100	130	150	130	61	1160	1200
3-Ethylphenol	250	230	190	220	270	520	62	4773	5200
4-Ethylphenol	270	230	330	340	810	690	690	2666	1400
2,3-Dimethylphenol	2300	2300	6200	2700	2700	6900	7300	17220	17500
2,4-Dimethylphenol	4200	4200	7200	3800	4100	9800	5800	21128	22500
2,5-Dimethylphenol	1100	1300	2900	1100	1200	3100	2400	10454	11200
2,6-Dimethylphenol	1200	1200	2900	1100	1100	2600	3100	4802	5100
3,4-Dimethylphenol	490	530	710	500	550	1400	490	4209	4600
3,5-Dimethylphenol	320	410	870	380	400	1100	690	2686	3300
2,3,5-Trimethylphenol	270	270	700	260	280	650	800	1414	1500
2,3,6-Trimethylphenol	150	170	350	140	150	340	410	967	930
2,4,6-Trimethylphenol	560	590	1500	540	520	1400	1600	3290	3300
3,4,5-Trimethylphenol	20	24	47	22	22	51	59	91	98
1-Naphthol	37	40	56	46	53	82	110	53	71
2-Naphthol	37	38	62	43	51	80	90	83	1300
Phenols	12 024	12 332	24 420	11 903	12 988	29 080	23 806	85 283	92 239

Table 2

Chemical contaminations of water recorded from 2010.04.26 to 2010.06.14 [mg/m³]

Parameter	04.26	04.26	05.10	05.10	05.27	05.27	06.07	06.07	06.14
	Raw water	Bioreactor	Raw water	Bioreactor	Raw water	Bioreactor	Raw water	Bioreactor	Raw water
Toxicity [TU]	400	47.6	153.8	66.7	125.0	15.2	111.1	62.5	133.3
TOC	144	33.0	167	33.3	143	31.9	142	33.5	145
MAH	10836	607.1	8555	128.4	6184	228.7	5274	244	9928
Phenol	190	12	330	13	84	60	86	65	<1.0
2-Methylphenol	2500	3.5	3400	6.6	2400	3.7	2448	3.9	1300
3-Methylphenol	4500	2.5	5100	1.7	3800	2.1	3876	2.2	2600
4-Methylphenol	7200	4.6	9000	4.7	6400	6.6	6528	7.1	3800
2-Ethylphenol	1400	3.8	1400	5.2	1600	6.6	1632	7.0	1200
3-Ethylphenol	6000	<1.0	7100	<1.0	6600	<1.0	6732	<1.0	4700
4-Ethylphenol	4000	32	8700	65	5500	219	5610	233	3300
2,3-Dimethylphenol	23300	560	24100	580	17400	2200	17748	2347	13800
2,4-Dimethylphenol	25700	5.4	28400	19	27200	14	27744	15	19800
2,5-Dimethylphenol	14100	14	12900	39	12000	150	12240	160	10000
2,6-Dimethylphenol	5700	1300	5500	1200	5700	1600	5814	1707	4400
3,4-Dimethylphenol	5700	4	6300	7.4	5500	8.6	5610	9.2	4100
3,5-Dimethylphenol	3900	13	3400	12	3800	34	3876	36	2900
2,3,5-Trimethylphenol	1700	150	1100	132	1700	350	1734	373	1400
2,3,6-Trimethylphenol	1100	150	690	150	1200	180	1224	192	970
2,4,6-Trimethylphenol	3500	630	2200	590	4000	790	4080	843	3300
3,4,5-Trimethylphenol	110	15	91	12	120	32	122	34	88
1-Naphthol	53	1.6	15	3.1	22	7.3	22	7.8	<1.0
2-Naphthol	84	<1.0	42	4.1	150	24	153	25	<1.0
Phenols	110 737	2901	119 768	2843	105 176	5687	107 280	6068	77 658

To identify the group of compounds or a single compound being responsible for the toxicity of the groundwater, use was made of statistical analysis, which entailed the results of toxicological and instrumental analyses (Tables 1, 2). The aim was to define the correlation between the results of toxicological analyses and the concentrations of particular polluting species occurring in the sample. The study was carried out in two stages. The former one was targeted at the correlations between the values obtained from toxicological analyses and the concentrations of main pollutants, i.e. total organic carbon (TOC), monoaromatic hydrocarbons (MAH) and phenols.

Use was made of four statistical models: linear, exponential, reciprocal and multiplicative, because a great number of biological processes are characterized by such relations (Table 3). Furthermore, models of that type justify the use of the least squares method, and consequently (owing to the available statistical tests) enable qualitative verification of the econometric model obtained. The regression models

(Table 3) clearly indicate that the relation between *TU*, TOC and phenols follows an evidently nonlinear trend, and that the type of this nonlinearity is closest to that of the multiplicative trend (as can be inferred from the values of the coefficients of determination R^2). The number of statistical samples was insufficient to clearly define the trend for the relationship between *TU* and MAH.

Table 3

Regression models for the relation between toxicity [TU] and concentrations of TOC, MAH and phenols in groundwater

Variable	Model			
	Linear $y = a + bx$	Exponential $y = e^{a + bx}$	Reciprocal $1/y = a + bx$	Multiplicative $y = ax^b$
TU/TOC	$y = -1.78 + 1.19x$ $R^2 = 52.3\%$ $(r = 0.723)$	$y = e^{3.25 + 0.01x}$ $R^2 = 70\%$ $(r = 0.83)$	$1/y = 0.034 - 0.0002x$ $R^2 = 45\%$ $(r = -0.67)$	$y = 1.68x^{0.9604}$ $R^2 = 66.5\%$ $(r = 0.81)$
TU/MAH	$y = 45 + 0.0074x$ $R^2 = 20\%$ $r = 0.43$	$y = e^{(3.78 + 0.000068x)}$ $R^2 = 21\%$ $r = 0.46$	$1/y = 0.026 - 0.00000107x$ $R^2 = 15\%$ $(r = -0.39)$	$y = 295x^{0.22}$ $R^2 = 18.5\%$ $(r = 0.43)$
TU/Phenols	$y = 28051 + 0.0015x$ $R^2 = 55.57\%$ $(r = 0.745)$	$y = e^{3.59 + 0.0000148x}$ $R^2 = 68\%$ $(r = 0.82)$	$1/y = 0.028 - 0.000000216x$ $R^2 = 42\%$ $(r = -0.65)$	$y = 0.55x^{0.449}$ $R^2 = 53\%$ $(r = 0.72)$

Tables 4 and 5 show the values of the coefficient of correlation between *TU*, TOC, MAH and phenols. Based on those values, it can be assumed that the correlation coefficients for *TU* and TOC, as well as for *TU* and phenols, take significant values and thus characterize a significant trend for a linear dependence. However, the data in Table 3 make it clear that the exponential trend is more adequate because of a higher coefficient of correlation and, also, R^2 . Hence, if the coefficient of correlation takes a high value, this does not exclude the possibility of obtaining a higher one. The key issue consists in tracing the right trend. The research conducted by other authors [13] proved, that statistical analysis can be efficiently used in tracing such trend for aims of toxicology.

Table 4

Significance levels for the correlation coefficients

x_i	y_i	
	Toxicity [TU]	Significance level
TOC	0.7232	0.0007
MAH	0.4379	0.0691
Phenols	0.7454	0.0004

Table 5

Significance levels for the correlation coefficients

Parameter	TOC	MAH	Phenols
TOC	1 (18) $p = 0$	0.48 (18) $p = 0.044$	0.97 (18) $p = 0$
MAH	0.48 (18) $p = 0.044$	1 (18) $p = 0$	0.40 (18) $p = 0.098$
Phenols	0.97 (18) $p = 0$	0.40 (18) $p = 0.098$	1 (18) $p = 0$

Analysis of the relationship between the parameters characterizing the concentrations of the chemical compounds occurring in the water sample used in this study has revealed a close correlation between the result for TOC and the result for phenols (Table 5). The results of statistical analysis indicate that phenols were responsible for the toxicity of the groundwater polluted by gasworks.

Table 6

Regression analysis: exponential model $Y = \exp(a + bX)$

Dependent variable – toxicity, independent variable – 2,3-dimethylphenol				
Parameter	Estimate	Standard error	<i>t</i> -value	Probability level
Intercept	3.52538	0.166789	21.1357	0.00
Slope	0.00008	0.000013	5.98636	0.00002
Correlation coefficient – 0.831467				
Standard error of estimation – 0.462556				
$R^2 = 69.13\%$				

The aim of the latter stage was to establish which of the compounds belonging to the group of phenols was directly responsible for the toxicity of the groundwater being tested. Analysis was carried out for 15 compounds detected in the sample (phenol, methylphenols, dimethylphenols, trimethylphenols and naphthols) (Tables 1, 2). The calculated results indicate that 2,3-dimethylphenol was responsible for the toxicity of the samples; the rise in the concentration of this compound was best correlated with the toxicity of the groundwater (Table 6). This dependence was established when the linear regression model was constructed using the stepwise variable selection forward method. The stepwise variable selection backward method produced the same result. Both the methods are widely used for this purpose and have been verified in engineering applications. In this study, the most satisfactory equation was obtained for the exponential relation.

4. SUMMARY

The Microtox test was found to be a highly effective tool in assessing not only the extent of groundwater pollution from gasworks, but also the progress of the treatment process. The results obtained provide reliable information on the course of technological process of water treatment. Quick availability of the results of toxicological analyses makes it possible to correct the treatment process within a short time, and thus achieve the treatment effects desired. Furthermore, it has been demonstrated that in the case of environmental samples, when use is made of statistical methods, it is possible to make a decision which compound being a component of the mixture is the main contributor to the toxicity of the sample examined. Any other analyses, even those of high accuracy, fail to offer such possibilities. Toxicity tests have the capacity for providing them, because they incorporate the interaction between particular components of the mixture of compounds that pollute the groundwater sample.

Owing to its wide use, the Microtox test has become not only an effective tool for assessing the concentrations of model substances, but also an excellent screening method. Such method may prove useful when quick decisions are to be made about the technological process or the environment. It is essential to note that for reasons resulting from the environmental regulations being currently in force, as well as for technical and economic reasons, standard assessments of water and wastewater quality do not include many groups of pollutants whose concentrations are low. However, these concentrations may increase sporadically – and then a quick toxicity test becomes invaluable in minimizing the environmental risk.

5. CONCLUSIONS

The Microtox system is a useful tool for assessing the progress of the biological treatment process for groundwater polluted by gasworks.

Phenols, and specifically 2,3-dimethylphenol whose concentration increases in best correlation with water toxicity, were found to be responsible for the toxicity of the groundwater sample.

When use is made of statistical methods, it is possible not only to determine the relation between toxicity and the concentrations of the compounds being components of the pollutants, but also to identify the compound responsible for the toxicity water.

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