

Safety analysis of the wastewater treatment process in the field of organic pollutants including PAHs

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ABSTRACT

The main goal of this work is to show the approach to determining safety of the wastewater treatment process. Household or municipal treated wastewaters discharged into waters should not exceed the maximum acceptable values of pollution indicators or should be treated at least to such degree that they meet the minimum percentage of pollution reduction specified in the current standards. Safety of the wastewater treatment process (SWsTP) is defined as a condition in which the process meets all the specified standards and is characterized by resistance, the ability to avoid hazards and exposures. In this paper, however, the proposal of a method for analysis and assessment of SWsTP, based on a risk analysis of the technological unreliability of the sewage treatment plant, in relation to the biodegradable organic pollutants expressed by the BOD₅ indicator, with particular emphasis on toxic organic micro-pollutants which are polycyclic aromatic hydrocarbons (PAHs), is presented. The presented method allows to take into account different levels of exceeding the maximum permissible load and scales resulting from the different probability of the occurrence of individual states. The concept was studied on the basis of real data from the wastewater treatment plant.

Keywords: Wastewater treatment process; Safety; Risk; BOD₅; PAHs-EPA

1. Introduction

The European Union standards regarding the quality of municipal wastewater discharged into water determines the Council Directive 91/271/EEC of 21 May [1]. As part of the Polish accession to the European Union the commitments of this document were adopted. In order to identify the needs in the field of wastewater management and the order of taking necessary actions the National Programme for Urban Wastewater Treatment (NPUWT) was developed. The program was approved in 2003. In 2005 the first update of the program (UNPUWT) was made and until now the fourth update was approved. The current document contains, among others, an action plan to year 2021 and includes ensuring the removal of nutrients from

wastewaters in agglomeration with a size of more than 10,000 population equivalents (PE) [1,2].

The acceptable values depend on the size of the treatment plant which is expressed by a special indicator called population equivalents (PE) or equivalent number of inhabitants. This indicator is calculated based on the maximum weekly average concentration of organic impurities expressed by an indicator of a five-day biochemical oxygen demand BOD₅, the individual pollution load produced by one person per day (60 g/M·d) [3,4] and the amount of wastewater flowing into the treatment plant during a year, excluding unusual situations, in particular resulting from heavy rainfall. The load of newly built, expanded or rebuilt sewage treatment plant is taken from the design assumptions.

General standards of the EU [1] on the municipal treated wastewaters in agglomerations indicate five basic indicators characterizing their quality. Two of them relate

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to the contents of organic compounds denoted by general indicators such as BOD₅, COD, and the remaining are: total suspended solids, total nitrogen N_{og} and total phosphorus P_{og}. It should be emphasized that the organic compounds are also included in the total suspended solids, total nitrogen and total phosphorus, respectively, organic nitrogen and organic phosphorus. The restrictions for nutrients do not apply to all sewage disposal facilities (when the receivers are waters susceptible to eutrophication, wastewater treatments for which PE < 2000). The Directive also specifies the essential values of the probability of exceeding and maintaining the requirements depending on the number of samples taken for testing, which, in turn, depends on the size of the PE [1]. The Polish legislation also determines the frequency of sampling for analyses and a list of reference analytical methods recommended for use during these analyses. 16 toxic compounds and 59 other indicators of pollution are also listed [3]. For the five basic indicators of the quality of wastewater discharged into the environment as the outflow from the wastewater treatment plant, such as BOD₅, COD, total suspended solids, total nitrogen and total phosphorus, the acceptable concentration and the minimum degree of the removal of impurities expressed by these indicators, are given. For BOD₅, COD, total suspended solids, the concentrations which may be exceeded in 75–95% of cases a year, are also given. In the current regulation on treated wastewaters the permissible concentrations of PAHs are not given, but these compounds are among those that should be eliminated from wastewaters [3].

Safety of the wastewater treatment process (SWsTP) is defined as a condition in which the process meets all the specified standards and is characterized by resistance, the ability to avoid hazards and exposures. The analysis of such defined SWsTP is made from the point of view of safety for the wastewater receiver. The measure of SWsTP is the risk associated with the technological unreliability of the wastewater treatment plant [5–6]. The current standards for safety analysis in the widely understood water management include the processes associated with the so-called Water Cycle Safety Plans [7]. These plans assume the risk analysis of threats at every stage of the water cycle in the basin of the city and should be a primary tool for risk management [8].

Danger and hazard are the factors that determine the magnitude of the risk. Danger is considered a cause of loss. Hazard as a risk factor determines the magnitude of losses resulting from occurred risk [8–9]. Excesses over the limits concentrations of treated sewage can cause elevated values in the receiver. As a result, the receiver as a source of water can be a hazard for the water consumer or forces more extensive water treatment process.

Risk analysis is conducted to determine the risk by estimating the probability of the occurrence of undesirable events and their consequences [5]. The risk was estimated based on the assumption that the higher the standard deviation from the average value of permissible concentrations of pollutants, the greater the risk associated with the probability of undesirable events occurrence, for example, exceeded permissible concentrations of pollutants in the treated wastewater. In this sense, the risk is interpreted as the expected value of losses associated with the occurrence of an undesirable event, such as wrongly designed or executed waste water treatment process [6].

Risk management within the normal operation of sewage treatment plants should contain [8]:

- The SWsTP analysis: in order to determine whether the process of wastewater treatment provides health and ecological goals accordance with the applicable directives and standards. It should include an analysis of pollutants covered by the standard guidelines for the receiver of waste water as well as micro-contaminants that may pose a threat to the entire water cycle in urban catchment, for example, polycyclic aromatic hydrocarbons (PAHs).
- Identification of potential risks: including identification of potential development of paths threats.
- Assessment of the risk management measures: for each control procedure should be an appropriate system of operational monitoring.
- Documentation of risk: plans describe the measures to be taken during normal operation or during the hazard (e.g. exceeding the concentration of specific indicators of pollution effluent from sewage).

2. Purpose and scope of work

Analysis and assessment of the safety of municipal water supply systems can be found, among others, in the works [5–9]. In this paper, however, the proposal of a method for analysis and assessment of SWsTP based on a risk analysis of the technological unreliability of the sewage treatment plant, in relation to the biodegradable organic pollutants expressed by the BOD₅ indicator, with particular emphasis on toxic organic micro-pollutants which are polycyclic aromatic hydrocarbons (PAHs), is presented.

3. Characteristics of municipal wastewaters in terms of organic pollutants including PAHs

3.1. Characteristic of wastewater

Experience in designing and operation of the sewage treatment plants indicate that there are no typical municipal wastewaters, as chemical characteristics of wastewaters from different agglomerations and other units is different. Therefore, in the literature data the pollution indicators are divergent. The average values of indicators are adopted for designing and calculations, but in real life the identified values often significantly differ from the assumptions. In the case of a general indicator of organic pollutants which is BOD₅, the assumed average value is 300 mg O₂/L. The exemplary values of BOD₅ and other indicators are presented in Table 1.

3.2. Hazardous characteristics of PAHs

Among the organic pollutants the special importance have polycyclic aromatic hydrocarbons PAHs. This is due to the toxic influence of these compounds on the organisms. Toxicological studies confirmed carcinogenic, mutagenic and teratogenic effects of these compounds [14–16].

The US Environmental Protection Agency EPA indicates 16 compounds which should be analyzed in the environment. In the literature are described studies in which differential number of these compounds is donated (six, eight, eleven, sixteen) [17]. Therefore, a comparison of total concentration in the studied matrices is not always possible. Toxicological studies have shown different impact of PAHs on organisms. The International Agency for Research on Cancer (IARC) divided chemicals into groups, depending on their potential carcinogenic properties, which are as follows [18]:

- Group 1 – carcinogenic factors,
- Group 2A – probably carcinogenic factors,
- Group 2B – potentially carcinogenic factors,
- Group 3 – factors not classified as carcinogenic,
- Group 4 – probably not carcinogenic factors.

3.3. The presence of PAHs in municipal wastewater treated in the conventional WsTP

Previous studies confirm the presence of these compounds in household, rainfall and industrial wastewaters. In municipal wastewaters the PAHs concentration level depends on the participation and type of industrial

wastewaters and sewerage system (combined, separate). Especially highly loaded by those compounds are industrial wastewaters from fuel processing (e.g. coke, refining), metallurgical, rain runoff from important roads and land-fill leachates. Table 2 shows the PAH contents in raw and treated municipal wastewaters [19–28].

In municipal wastewaters the PAHs total concentrations given in the cited literature reach 28 µg/L. Most data, however, have values of a few micrograms per litre of wastewater. In the highest concentrations are generally hydrocarbons, 2- and 3-ring compounds, regardless the degree of purification. Due to the lipophilic properties the PAHs in wastewater are mainly found in the form adsorbed in the suspended solids [27,28]. The concentration of PAHs in sewage sludge reached 3mg/kg d.m. [26–28]. However, in a dissolved form they may sometimes be present in concentrations above the solubility, due to the presence of other compounds, such as, for example, surfactants [18,22]. Reports in the literature and previous monitoring research showed that in the wastewater treatment processes the PAHs are not removed sufficiently and treated wastewaters bring to the receivers a substantial load of these compounds [19–21,25,26,29–31]. It is important that in the legal regulations concerning treated wastewaters the permissible concentrations of these compounds are not given, but they are only presented as the compounds that need to be eliminated from the wastewaters due to their toxic nature (List I) [3]. They are listed, however, in the legal regulations relating to the classification of waters and in monitoring studies of surface and underground waters [30]. Moreover, they are classified as priority substances for the aquatic environment and some of them as the priority dangerous substances and classified as persistent organic pollutants. Also the concentration of selected PAHs, (benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(g,h,i)perylene, indeno(1,2,3-cd)pyrene) in drinking water is standardized [20–22].

Table 1
Composition of the municipal wastewaters [4,10–13]

| Indicator | The average concentration | Range of concentration |
|---|---------------------------|------------------------|
| BOD ₅ , mg O ₂ /L | 295–430 | 90–600 |
| COD, mg O ₂ /L | 706–860 | 100–1,250 |
| Total suspended solids, mg/L | 360–395 | 120–500 |
| Total nitrogen, mg/L | 82–95 | 3–104 |
| Total phosphorus, mg/L | 10–20 | 4–23 |

n.d – no data

Table 2
The contents of PAHs in municipal raw and treated wastewaters [19–28]

| Treatment plant location | Capacity of treatment plant m ³ /d | Total PAH concentration µg/L | | References |
|--------------------------|---|--|-------------------------------|------------|
| | | Raw wastewater (influent) | Treated wastewater (effluent) | |
| Italy (Venice) | 90,000 | 4.6 | 1.1 | [19] |
| Italy (5 objects) | 12,000–700,000 | 0.14–1.54 | 0.08–0.2 | [20] |
| France (Paris) | 2,600,000 | 28 (63% adsorbed in suspended solids) | n.d | [21] |
| Norway (5 objects) | 10,000–120,000 | 1.2–1.3 | n.d | [22] |
| China | 300,000 | 5.7 | 2.2 | [23] |
| China (5 objects) | 200,000 | Summer: 0.33–0.43(3.4–5.1 mg/kg in suspended solids) Winter: 0.68–0.82(5.2–6.4 mg/kg in suspended solids) | n.d | [24] |
| Poland | 58,000–60,000 | 5.1–6.9 | 0.29–1.28 | [25,26] |
| Italy Lombardy region | 100,000 (70%-domestic, 30%-industrial) | 2.6–4.0 | n.d | [27,28] |

n.d – no data

4. Materials and methods

4.1. Analytical methods of PAHs

Wastewater samples from the municipal wastewater treatment plant were analysed for 16 EPA-PAHs [25,30]. This wastewater treatment plant consists of activated sludge technology with additional chemical treatment for the removal of phosphorus compounds. The following wastewater samples were taken: raw wastewater (influent) and treated wastewater (effluent). For PAHs extraction from wastewater samples liquid–liquid extraction was used. Based on the earlier investigations the mixture of methanol: cyclohexane: dichloromethane (v/v 30:5:1) was used as extracting agent [25]. Polarity of the extractants were equal to 0.34 and 6.6 for C_6H_{12} , CH_2Cl_2 and CH_3OH , respectively. Methanol was used as the agent for desorption of PAHs from solid. Organic matrix extraction was performed on the shaker with horizontal motion for 60 min. Then the extracts were separated from the wastewater samples in a laboratory separator, dried with anhydrous sodium sulphate and concentrated to 3 mL. After that the extracts were purified under vacuum conditions on silica gel. The silica gel bed was previously conditioned with cyclohexane: dichloromethane mixture. Cleaned extracts (with PAHs) were concentrated under nitrogen stream to 1 mL. The experimental procedure is presented in Fig. 1. To verify the method of wastewater samples preparation for PAHs analysis the con-

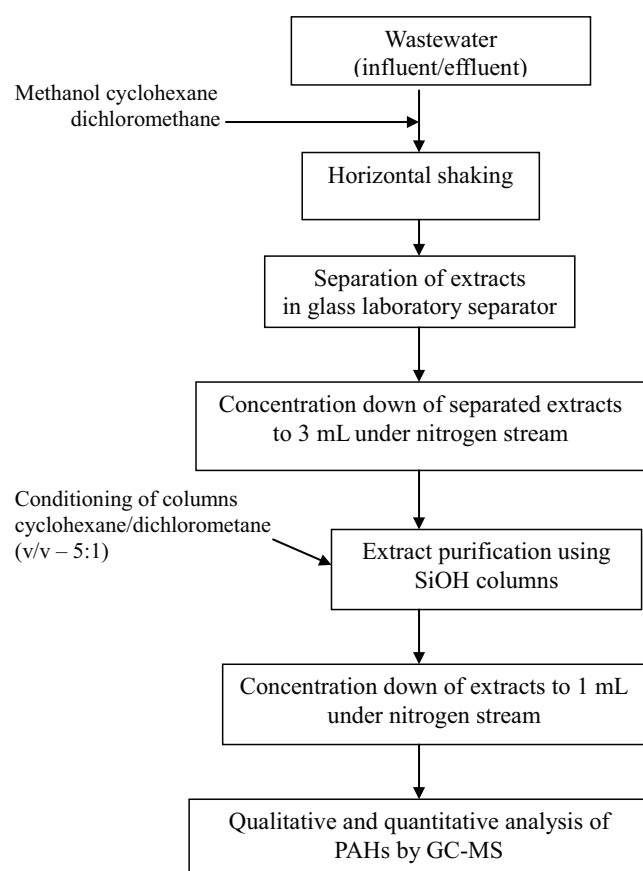


Fig. 1. Preparation of wastewater samples to determination of PAHs by GC-MS [30–33].

trol samples with known concentration of PAH compounds were prepared. Standard mixture of PAHs (not deuterated hydrocarbons) (Accu Standard Inc. USA - PAH Mix) in benzene and dichloromethane (v/v 1:1) was spiked into the influent and effluent samples. Standard mixture concentration spiked into the samples was equal to 30 $\mu\text{g/L}$.

For chromatographic determination of individual PAHs GC 8000 the gas chromatograph Fisons equipped with a mass spectrometric detector MD 800, was used. The parameters of chromatographic analysis were as follow: carrier gas - helium 70kPa, temperature program 40°C–120°C (40°C /min) to 280°C (5°C/min) and 280°C for 20 min, interface temperature – 280°C, column – DB-5 (30 m; 0.25 mm; 0.25 μm), integration system – MassLab. volume injection – 1 μL , injection system – on column injector. The extracts (in cyclohexane/dichloromethane) were directly introduced into the precolumn (1.5 m length). Limit of detection values for individual compounds were as follows: naphthalene – 0.14, acenaphthylene – 0.31, acenaphthene – 0.43, fluorene – 0.46, phenanthrene – 0.59, anthracene – 0.54, fluoranthene – 0.30, pyrene – 0.22, benzo(a)anthracene – 0.28, chrysene – 0.28, benzo(b)fluoranthene – 0.28, benzo(k)fluoranthene – 0.27, benzo(a)pyrene – 0.21, indeno (1,2,3,c,d) pyrene – 0.24, dibenzo(a,h)anthracene – 0.22, benzo(g,h,i), perylene – 0.20 ($\mu\text{g/L}$).

Recovery was calculated taking into the consideration both spiked PAHs concentration and initial concentration of individual compounds in the wastewater. PAHs recoveries varied between 48 and 95% and were in the range of 53–119% for influent and effluent, respectively. Both in treated and raw wastewaters the highest recovery values were obtained for hydrocarbons of water solubility (99%). Simultaneously high (over 97%) recoveries were obtained in the case of hydrocarbons with log K_{ow} in the range of 5 to 6. Average recovery of standard mixture (then volatile hydrocarbons are omitted) was high and reached 93% and 73% for influent and effluent, respectively.

In Table 3 the concentrations of 16 PAHs in wastewater are given.

The concentration of 16 PAHs in raw wastewater (influent) was on average 6.451 $\mu\text{g/L}$. The concentration of carcinogenic compounds is equal to 1.223 $\mu\text{g/L}$. The highest PAHs concentrations found in wastewater were naphthalene (28%) and phenanthrene (17%). The results correspond with literature data [19–24]. In the treated wastewater the total concentration of 16 PAHs and carcinogenic compounds were lower by 81% and 97%, respectively. It was due to the fact that hydrocarbons were accumulated onto solid matter (sewage sludges). In previous investigation were observed that PAHs' load drained off to the environment constituted approximately 37% of inflow to the wastewater treatment plant (15–17)% with treated wastewater, (19–22)% with stabilized sludges [26,33].

4.2. Reliability

Technological unreliability (TU) of the wastewater treatment plant is shown by the Eq. (1) [6]:

$$TU = \frac{L_{n.od.}}{L_{n.do.}} \quad (1)$$

where $L_{n.od.}$ – excessive daily load of organic impurities expressed by a general indicator BOD_5 and/or PAHs, at the

Table 3
Concentration of 16 PAHs in wastewater (influent and effluent), µg/L

| Non carcinogenic PAHs | Wastewater | | Carcinogenic PAHs | Wastewater | |
|-----------------------|------------|----------|-------------------------|------------|----------|
| | Influent | Effluent | | Influent | Effluent |
| Naphtalene | 1.829 | 0.852 | Benzo(a)anthracene | 0.245 | 0.009 |
| Acenaphthylene | 0.189 | 0.008 | Chrysene | 0.249 | 0.008 |
| Acenaphthene | 0.311 | 0.011 | Benzo(b)fluoranthene | 0.150 | 0.005 |
| Fluorene | 0.336 | 0.013 | Benzo(k)fluoranthene | 0.204 | 0.007 |
| Phenanthrene | 1.074 | 0.029 | Benzo(a)pyrene | 0.147 | 0.003 |
| Anthracene | 0.213 | 0.005 | Indeno(1,2,3-cd) pyrene | 0.101 | 0.003 |
| Fluoranthene | 0.704 | 0.017 | Dibenzo(a,h)anthracene | 0.032 | 0.002 |
| Pyrene | 0.572 | 0.018 | Benzo(ghi)perylene | 0.095 | 0.004 |

effluent from the treatment plant, $L_{n,do}$ – excessive daily load of organic impurities expressed by a general indicator BOD₅ and PAHs, at the influent to the treatment plant (load which should be reduced in the wastewater treatment plant).

Three characteristic cases are possible:

- 1) TU = 1 – the treatment plant does not work or shows totally insufficient efficiency, organic compounds are not removed sufficiently,
- 2) TU = 0 – there is no excessive load BOD₅/PAHs at the effluent, the sewage treatment plant is working properly,
- 3) 0 < TU < 1 – the sewage treatment plant works with lower efficiency in treating organic compounds.

On the basis of TU the sewage treatment plants are divided into the so-called safety classes (SC). Four SC were introduced, additionally in the first three categories two categories A and B were introduced, depending on the characteristics of the wastewater receiver. A – rivers with a flow rate equal to or higher than 0.5 m/s, B – slow flowing rivers, where the flow of water does not exceed 0.5 m/s.

Distinction between fast flowing rivers and slow flowing rivers is due to the fact that in fast flowing rivers oxygen conditions are better and there is a possibility that treated wastewaters are mixed with the receiver waters.

4.2.1. SC I

Mechanical – biological sewage treatment plants where treated wastewaters are discharged into the receivers for which, in a period of one year, it is permitted to maximum exceed the load of pollutants expressed by BOD₅ and Σ16 PAHs, with full removal of biogenic compounds and purification efficiency $\eta = 0.95$, in an amount:

- 1) TU = 0.1 for A and TU = 0.05 for B, at total duration of these incidents equal to, respectively, 60 d,
- 2) TU = 0.7 at total duration of such events equal to 3 days (duration of a single incident cannot exceed 0.33 d)
- 3) TU = 1.0 at a total break time in the plant's operation not exceeding 0.25 d.

4.2.2. SC II

Mechanical-biological sewage treatment plants for which, in a period of one year, it is permitted to maximum exceed the load of pollutants expressed by BOD₅ and Σ16 PAHs, with removal of organic carbon and purification efficiency $\eta = 0.90$, in an amount:

- 1) TU = 0.15 for A and TU = 0.1 for B, the total duration of these incidents equal to, respectively, 60 d
- 2) TU = 0.7 at a total duration of such events equal to 5 d (duration of a single incident cannot exceed 0.33 d)
- 3) TU = 1.0 at a total break time in the plant's operation not more than 1 d (the maximum duration of a single incident is not longer than 0.5 d).

4.2.3. SC II

Mechanical-biological sewage treatment plants for which, in a period of one year, it is permitted to maximum exceed the load of pollutants expressed by BOD₅ and Σ16 PAHs, with partial removal of organic carbon and purification efficiency $\eta = 0.75$, in an amount:

- 1) TU = 0.2 for A and TU = 0.15 for B, the total duration of these incidents equal to, respectively, 60 d.
- 2) TU = 0.7 at total duration of such events equal to 7 d (duration of a single incident cannot exceed 0.33 d)
- 3) TU = 1.0 at a total break time in the plant's operation not more than 1 d (the maximum duration of a single incident not longer than 0.5 d).

The probability that the value of pollution load will exceed a given value of the permissible load at the effluent from the wastewater treatment plant depends on the duration of these exceedings [36]. The presented method allows to take into account different levels of exceeding the maximum permissible load and scales resulting from the different probability of the occurrence of individual states. Considerations were performed for a unit of time equal to one year. The method takes into account durations T_{ij} of the occurrence of periods in which the threshold values (interval limit) of the unreliability indicator (TU = 0.05; 0.1; 0.15; 0.2; 0.7; 1.0) can appear. The probability of the occurrence of these states can be determined from the Eq. (2):

$$P_i = \frac{\sum_{j,k} T_{i,jk}}{365} \quad (2)$$

where $T_{ij,k}$ – a total duration for a given interval i ; i – next number of the interval, $i = 1, 2, 3$, according to the information given in the description of importance category of the sewage treatment plant; j – next number of subinterval (if there are subintervals), $j = 1, 2, \dots, s$; k – next number of existed case of time period in which given data TU_i are present in the j -th subinterval if they are not present, then, respectively, in i -th interval $k = 1, 2, \dots, m$; s – a total number of all considered subintervals; m – a number of all existed cases (at the relevant period of time).

While taking into account a total duration of cases in which given values T_i or T_{ij} occurred, then the Eq. (2) takes a simpler form:

$$P_i = \frac{\sum_j T_{ij}}{365} \quad (3)$$

In such case $T_{1,2}$ means the interval $i = 1$ and the subinterval $j = 2$. In such described duration of a given case, i.e. in case of TU_i , the total durations are considered as the sum of all the partitive cases. Analogous marks were adopted to determine the probability of the occurrence of given incidents, for example, $P_{1,1}$ relates to $i = 1$ and $j = 1$ and P_2 means that the interval 2 has not been divided into subintervals.

For states $TU = 0$, i.e. for the periods in which the permissible load in the effluent is not exceeded, the probability of their occurrence can be determined from the relation:

$$P_o = 1 - \sum_{i=1}^n P_i \quad (4)$$

where n – a number of considered intervals.

The factor showing the unreliability of the treatment plant regarding the quality of treated wastewater is an excess load of a given pollution indicator (e.g. BOD_5) over the permissible value specified indirectly by the value TU , occurring within a specified time period. The generalized unreliability is defined as a ratio of the expected value of exceeding of the indicator TU (cases where $TU > 0$), marked by a symbol $E(TU_i)$, to the limit value of this exceeding ($TU_{max} = 1$). It is defined as the relative risk of technological unreliability of the treatment plant. For one year it is expressed by the Eq. (5) [32]:

$$r_{wTU} = \frac{E(TU_i)}{TU_{max}} \quad (5)$$

where r_{wTU} – generalized unreliability; $E(TU_i)$ – the expected value; TU_{max} – technological unreliability in the considered case $TU_{max} = 1.0$ (efficiency of organic pollutants removal is at level 0).

Properly generalized indicator of the technological reliability (TR) of the treatment plant is [32–37]:

$$TR = 1 - r_{wTU} \quad (6)$$

and the expected value $E(TU_i)$ was determined as:

$$E(TU_i) = \int_{-\infty}^{\infty} TU_i f(TU_i) d(TU_i) = \frac{\sum_{i=1}^n P_i^c TU_i}{\sum_{i=1}^n P_i} \quad (7)$$

where n – a number of considered intervals.

Table 4 shows the permissible values of the indicator TR . From the engineering point of view, the value of the likelihood that the treated wastewaters discharged from the plant at any time will meet the assumptions, is important. Such case is described by a stationary indicator of technological reliability of the treatment plant (STR). This indicator refers to the case of $TU = 0$ and is equal to the value of P_o . The use of the data contained in the Table 4 means the necessity of calculating the values of TR and STR for each sewage treatment plant and checking whether there is a relation [38]:

$$STR > TR \quad (8)$$

where, TR – the permissible generalized indicator of technological reliability, STR – the stationary indicator of technological reliability.

5. Application example

Table 5 shows calculations for the assumed effects of wastewater treatment and their permissible values in view of the criterion TU for the computational interval $i = 1$, and when:

- concentration of sewage in effluent $BOD_5 = 360g O_2/m^3$,
- $\sum 16$ PAHs = 6.45 $\mu g/L$ (including carcinogenic compounds – 1.26 $\mu g/L$).

The degree of removal of these contaminants (purification efficiency η) was assumed at:

- complete biological purification with nitrification – purification efficiency $\eta = 0.95$,
- complete biological purification – purification efficiency $\eta = 0.90$,
- partial biological purification – purification efficiency $\eta = 0.75$.

Table 6 shows calculations for the assumed effects of wastewater treatment and their permissible values in view of the criterion $TU = 0.7$, assumed duration $TU = 1$ or $TU = 2$ or $TU = 3$ days, depends on SC.

We analysed the work of the mechanical and biological wastewater treatment plant SC II, which discharges sewage into the river with an average velocity of 0.6 m/s. Within one year we stated the following exceeding of BOD_5 loads in the effluent and their total durations:

- $TU_{11} = 0.05$; $T_{11} = 20$ days two computational intervals were taken $TU_{12} = 0.1$; $T_{12} = 35$ days
- $TU_2 = 0.5$; $T_2 = 1.2$ days one computational interval was taken
- $TU_3 = 1.0$; $T_3 = 1/24$ days one computational interval was taken.

The probability of the states P_i are as follows:

Table 4
The permissible values of technological reliability (TR)

| SC | | Cases of computing | | T_i | TU_i | P_i | $P_i TU_i$ | TR= $1-(P_1+P_2+P_3)$ | TR for $TU=0$ | TR for $TU=1$ | |
|-----|----|--------------------|-----------------|-----------------|--------|-------------|------------------------|--------------------------|------------------|------------------|----------|
| | | I | TU | d/365 | | | | | | | |
| I | A | 0 | $TU = 0$ | – | – | 0.832191 | | 0.9809589 | 0.8321918 | 0.16781 | |
| | | 1 | $0 < TU < 0.1$ | 60.0 | 0.1 | 0.1643835 | 0.01643835 | | | | |
| | | 2 | $0.1 < TU < 1$ | 1.0 | 0.7 | 0.00273972 | 0.001917804 | | | | |
| | | 3 | $TU = 1$ | 0.25 | 1 | 0.000684931 | 0.000684931 | | | | |
| | | | | | | | $\Sigma = 0.019041085$ | | | | |
| | B | 0 | $TU = 0$ | – | – | 0.832191 | | 0.9891781 | | | |
| | | 1 | $0 < TU < 0.05$ | 60.0 | 0.05 | 0.1643835 | 0.008219175 | | | | |
| | | 2 | $0.05 < TU < 1$ | 1.0 | 0.7 | 0.00274 | 0.001918 | | | | |
| | | 3 | $TU = 1$ | 0.25 | 1 | 0.000685 | 0.000685 | | | | |
| | | | | | | | $\Sigma = 0.010822175$ | | | | |
| | II | A | 0 | $TU = 0$ | – | – | 0.8287671 | | 0.970137 | 0.8287671 | 0.171233 |
| | | | 1 | $0 < TU < 0.15$ | 60.0 | 0.15 | 0.1643835 | 0.024657525 | | | |
| 2 | | | $0.15 < TU < 1$ | 2.0 | 0.7 | 0.00547945 | 0.003835615 | | | | |
| 3 | | | $TU = 1$ | 0.5 | 1.0 | 0.0000137 | 0.0000137 | | | | |
| | | | | | | | $\Sigma = 0.02850684$ | | | | |
| B | | 0 | $TU = 0$ | – | – | 0.8287671 | | 0.9783562 | | | |
| | | 1 | $0 < TU < 0.1$ | 60.0 | 0.1 | 0.1643835 | 0.01643835 | | | | |
| | | 2 | $0.1 < TU < 1$ | 2.0 | 0.7 | 0.00547945 | 0.003835615 | | | | |
| | | 3 | $TU = 1$ | 0.5 | 1.0 | 0.0000137 | 0.0000137 | | | | |
| | | | | | | | $\Sigma = 0.020287665$ | | | | |
| III | | A | 0 | $TU = 0$ | – | – | 0.8253435 | | 0.959315 | 0.8253425 | 0.174657 |
| | | | 1 | $0 < TU < 0.2$ | 60.0 | 0.2 | 0.1643835 | 0.0328767 | | | |
| | 2 | | $0.2 < TU < 1$ | 3.0 | 0.7 | 0.00821917 | 0.005753419 | | | | |
| | 3 | | $TU = 1$ | 0.75 | 1.0 | 0.00205479 | 0.00205479 | | | | |
| | | | | | | | $\Sigma = 0.040684909$ | | | | |
| | B | 0 | $TU = 0$ | – | – | 0.8253435 | | 0.9675343 | | | |
| | | 1 | $0 < TU < 0.15$ | 60.0 | 0.15 | 0.1643835 | 0.024657525 | | | | |
| | | 2 | $0.15 < TU < 1$ | 3.0 | 0.7 | 0.00821917 | 0.005753419 | | | | |
| | | 3 | $TU = 1$ | 0.75 | 1.0 | 0.00205479 | 0.00205479 | | | | |
| | | | | | | | $\Sigma = 0.032465734$ | | | | |

$$\left. \begin{aligned} P_{11} &= \frac{20}{365} = 0.0547945 \\ P_{12} &= \frac{35}{365} = 0.0958904 \end{aligned} \right\} P_1 = \sum P_{ij} = 0.1506849$$

$$P_2 = \frac{1.2}{365} = 3.28767 \cdot 10^{-3}$$

$$P_3 = \frac{1}{365} = 1.14155 \cdot 10^{-4}$$

$$P_o = 1 - 0.1540864 = 0.8450132 = STR$$

Because $STR = 0.8450132 > 0.8287671$, a condition for correct operation is met. Calculation of the generalized indicator of reliability STR

$$\begin{aligned} P_{11} TU_{11} &= 0.0547945 \cdot 0,05 &= 2.73972 \cdot 10^{-3} \\ P_{12} TU_{12} &= 0.0958904 \cdot 0,1 &= 9.58904 \cdot 10^{-3} \\ P_2 TU_2 &= 3.28767 \cdot 10^{-3} \cdot 0,5 &= 1.64383 \cdot 10^{-3} \end{aligned}$$

$$P_3 TU_3 = 1.14155 \cdot 10^{-4} \cdot 0,1 = 1.14155 \cdot 10^{-4}$$

$$\Sigma 0.0140867$$

Therefore:

$$TR = 1 - r_{wTU} = 1 - 0.0140867 = 0.9859132$$

Because the condition is satisfied, $0.9859132 > 0.970132$, so it can be stated that the analysed wastewater treatment plant meets the requirements SC II and meets the requirements for the assumed effect of wastewater treatment.

Operating conditions for the technological unreliability $TU = 0.05, 0.1, 0.15$ and 0.2 were determined for the climatic conditions in Central and Eastern Europe (winter period lasts about 60 d). Failure to comply with this restriction requires an analysis of the temperature of the process of biological wastewater treatment and the adjustment of time criterion for the assumed value of TU for each SC.

Table 5

Calculations for the assumed effects of wastewater treatment and their permissible values in view of the criterion TU for the computational interval $i = 1$, assumed duration $TU = 60$ days

| SC | Sewage receivers | Computational case for biological process Efficiency | The expected effects of wastewater treatment expressed by | | | The permissible values of effects of sewage treatment plant at a given limit of the duration, expressed by $T = 60$ days | | |
|------|------------------|--|---|--------------------|--------------|--|--------------------|--------------|
| | | | Removal % | BOD ₅ * | PAHs * | Removal % | BOD ₅ * | PAH* |
| TU | | | $TU = 0$ | | | $TU = 0.1$ | | |
| I | A | A | 95 | 18 | 0.32 (0.063) | 85.5 | 52.2 | 0.94 (0.183) |
| | | B | 90 | 36 | 0.65 (0.126) | 81.0 | 68.4 | 1.23 (0.239) |
| | | C | 75 | 90 | 1.61 (0.315) | 67.5 | 117 | 2.10 (0.410) |
| TU | | | $TU = 0$ | | | $TU = 0.05$ | | |
| I | B | A | 95 | 18 | 0.32 (0.063) | 94.5 | 19.71 | 0.35 (0.069) |
| | | B | 90 | 36 | 0.65 (0.126) | 89.6 | 37.62 | 0.67 (0.13) |
| | | c | 75 | 90 | 1.61 (0.315) | 74.6 | 91.35 | 1.64 (0.320) |
| TU | | | $TU = 0$ | | | $TU = 0.15$ | | |
| II | A | a | 95 | 18 | 0.32 (0.063) | 80.8 | 69.3 | 1.24 (0.242) |
| | | b | 90 | 36 | 0.65 (0.126) | 76.5 | 84.6 | 1.52 (0.296) |
| | | c | 75 | 90 | 1.61 (0.315) | 63.8 | 130.5 | 2.33 (0.456) |
| TU | | | $TU = 0$ | | | $TU = 0.1$ | | |
| II | B | a | 95 | 18 | 0.32 (0.063) | 85.5 | 52.2 | 0.94 (0.183) |
| | | b | 90 | 36 | 0.65 (0.126) | 81.0 | 68.4 | 1.23 (0.239) |
| | | c | 75 | 90 | 1.61 (0.315) | 67.5 | 117.0 | 2.1 (0.41) |
| TU | | | $TU = 0$ | | | $TU = 0.2$ | | |
| III | A | a | 95 | 18 | 0.32 (0.063) | 76.0 | 86.4 | 1.55 (0.302) |
| | | b | 90 | 36 | 0.65 (0.126) | 72.0 | 100.8 | 1.81 (0.353) |
| | | c | 75 | 90 | 1.61 (0.315) | 60.0 | 144.0 | 2.58 (0.504) |
| TU | | | $TU = 0$ | | | $TU = 0.15$ | | |
| III | B | a | 95 | 18 | 0.32 (0.063) | 80.8 | 69.3 | 1.24 (0.242) |
| | | b | 90 | 36 | 0.65 (0.126) | 76.5 | 84.6 | 1.52 (0.296) |
| | | c | 75 | 90 | 1.61 (0.315) | 63.8 | 130.5 | 2.33 (0.456) |

BOD₅ - concentration of sewage in effluent, mg O₂/L

PAH* (Carcinogenic compounds) – concentration of 16 PAHs in effluent, µg/L

Table 6

Calculations for the assumed effects of wastewater treatment and their permissible values in view of the criterion $TU = 0.7$, assumed duration $TU = 1$ or $TU = 2$ or $TU = 3$ days depends on SC

| Computational case for biological process efficiency | The expected effects of wastewater treatment expressed by | | | The permissible values of effects of sewage treatment plant at a given limit of the duration, expressed by $T = 1$ days for SC I or $T = 2$ days for SC II and $T = 3$ days for SCIII | | |
|--|---|--------------------|--------------|---|--------------------|--------------|
| | Removal % | BOD ₅ * | PAHs* | Removal % | BOD ₅ * | PAH* |
| $TU=0$ | | | | $TU = 0.7$ | | |
| a | 95 | 18 | 0.32 (0.063) | 28.5 | 257.4 | 4.61 (0.901) |
| b | 90 | 36 | 0.65 (0.126) | 27.0 | 262.8 | 4.71 (0.920) |
| c | 75 | 90 | 1.61 (0.315) | 22.5 | 279 | 5.00 (0.977) |

Failure to comply with the conditions associated with $TU = 0.7$ and $TU = 1$ should be a signal to analyse the modernization of the process of biological wastewater treatment or to consider its expansion.

6. Conclusions

- The treated wastewater discharged into waters should not exceed the maximum acceptable values of pollution indicators or should be treated at least to such degree that meet the minimum percentage of pollution reduction specified in the current standards.
- The proposed method can be used to analyse the risk associated with the possibility of exceeding the pollution loads in treated sewage depending on a way of the wastewater treatment process. It can be adapted for each type of pollution. Very important in the proposed approach is to analyse the duration of pollutant load exceeding, which enables the assessment of the effect of treatment in view of safety of the sewage receiver.
- To contribute towards safety of the wastewater treatment process, the methodology presented in the paper can be applied in the daily functioning of the wastewater treatment plant, in cooperation between engineers and operators.
- The real concentration of PAHs in the treated wastewater was less than the value calculated in most cases. The concentration of 16 PAHs in the treated wastewater (effluent) does not exceed $1\mu\text{g/L}$. Taking into account the amount of treated wastewater, the load of PAH discharges may be in the range of several dozen kilograms per year (including carcinogenic compounds). It is important because the hydrocarbons have toxic effects on aquatic organisms.
- The advantage of the presented in this work method for the analysis of safety of the sewage treatment plant is the use of practical limitation of the duration of an undesirable event (exceeding of specified concentrations of pollutants in treated wastewater). It is also important that this method takes into account assumed limits of TU in the technological process.
- The method can be used in the decision-making process regarding the modernization of the technological process. It should be remembered, however, that the assumed limits for the duration of the undesirable event and TU should be adapted to the local climatic conditions and regimes for sewage receiver.

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