*Desalination and Water Treatment*
www.deswater.com
doi: 10.5004/dwt.2023.29228

288 (2023) 197–207
March

# Water pollution risk assessment resulting from leaching organic micropollutants from sewage sludge

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Received 23 November 2022; Accepted 15 December 2022

**ABSTRACT**

One of the methods of managing biochemically stabilized sewage sludge is their implementation to soil. It is a method regulated by law specifying the requirements that must be met, concerning the level of soil contamination and sewage sludge. It is related to selected heavy metals as well as to sewage sludge and also to the presence of pathogenic organisms. Sewage sludge introduced into the soil performs the role as an organic fertiliser enriching the soil with nutrients. Nevertheless, sewage sludge, apart from valuable components, also contains persistent organic micro pollutants. During agricultural use of sewage sludge, they are introduced into the soil and may have a negative impact on the soil microflora development. They can also permeate into plants, which consequently creates the risk of food contamination as food pollutants . This is important because some of them demonstrate carcinogenic, mutagenic and teratogenic effects for living organisms, including humans. There are legal regulations in EU countries on the agricultural use of sewage sludge including micro-pollutants: polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCB) components, adsorbable organic halogens, di (2-ethylhexyl) phthalates, polychlorinated dibenzodioxins/dibenzofurans, linear alkylbenzene sulfonates and nonylphenol and nonylphenol ethoxylate substances. In fact, Poland has not imposed an obligation to control these organic micro pollutants in sewage sludge intended for agricultural use yet. The objective of this study is to assess the potential risk associated with leaching of selected organic micro-pollutants from sewage sludge under conditions reflecting the effect of atmospheric precipitation during storage or while naturally using the sewage sludge. Leaching tests were conducted according to the procedure for drawing up aqueous extracts. Micropollutants such as PAHs and PCBs in aqueous extracts from sewage sludge and soil mixtures with sewage sludge were analysed.

*Keywords:* PAHs; PCB; Sewage sludge; Aqueous extracts; Risk assessment

## 1. Introduction

The use of sewage sludge for environmental purposes (agriculture and land remediation) is one of the methods of its disposal [1]. This is a method regulated by law specifying the requirements that must be met. These requirements concern both the level of soil contamination and sediments with selected heavy metals such as: lead, cadmium, mercury, nickel, zinc, copper, chromium. For sediments, the presence of pathogenic organisms such as *Ascaris* sp., *Trichuris* sp., *Toxocara* sp. and *Salmonella* sp. was determined, as well as pH limit, dry matter content, organic matter content, total nitrogen, ammoniacal nitrogen, total phosphorus, calcium and magnesium. On the other hand, the tests of soils in which

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*Presented at the 15th Scientific Conference on Micropollutants in the Human Environment, 14–16 September 2022, Częstochowa, Poland*

municipal sewage sludge is to be used include the determination of pH value, content of available phosphorus per $P_2O_5$ and heavy metals content, as in the case of sediments. During the determination of the permissible dose of municipal sewage sludge used for agricultural purposes and land remediation, the principles of good agricultural practices shall be considered [2]. This includes the need to adjust the dose of municipal sewage sludge in terms of nitrogen and phosphorus content to the nutritional needs of plants, considering the use of fertilisers, crop aids and soil improvers. Therefore, taking legal conditions into account, the natural use of sludge is only possible in certain cases [3]. Usually, only the sludge from few facilities meets the conditions for use in agriculture. These are mostly sludges extracted from the domestic sewage discharged by small settlement units, with a small share of industrial sewage, excluding metal processing plants. This applies only to sludges that were previously biochemically stabilized, in accordance with the Directive 98/15/EC introducing the obligation to process sewage sludge [4,5]. Sewage sludge introduced into the soil acts as an organic fertiliser enriching the soil with nutrients [4]. However, sewage sludge, in addition to components that are useful for plants, such as nitrogen or phosphorus, also contains heavy metals and persistent organic pollutants, such as PAHs, PCBs and other halogen-organic compounds [5–7]. Thus, during the agricultural use of sludge, they are introduced together into the soil, creating a danger of contamination of plants and, consequently, contamination of food with these pollutants. This is important because some of these substances have known carcinogenic, mutagenic and teratogenic properties [8–10]. It has been proven that these compounds are available for plants and accumulate in various parts, which is confirmed in the literature and in earlier co-authored studies [11,12]. In addition, the sludge introduced into the soil may adversely affect the development of soil microflora [13]. However, the results of the research described in the literature are diverse and also include the results indicating the possibility of enriching the soil microflora by sewage sludge and increasing the possibility of degradation of organic xenobiotics. However, tests are usually carried out under laboratory conditions, on selected cultures of bacteria, and using one or more hydrocarbons. This does not reflect the actual conditions where PAHs or PCBs are present in the mixture and the soil is populated with microorganisms of different composition and properties. The amendment to the Sludge Directive introduced in some countries of the EU concerns compounds such as polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyl (PCB) components, adsorbable organic halogens, di(2-ethylhexyl) phthalates, polychlorinated dibenzodioxins/dibenzofurans, linear alkylbenzene sulphonates, and nonylphenol and nonylphenol ethoxylate substances [14]. In Table 1, the proposed limit values for these pollutants are given [14,15].

To date, however, no legal obligation has been imposed in Poland to control these organic micropollutants in sludge intended for agricultural use. In addition to contamination of the soil with pollutants present in the sewage sludge, there is a potential risk of contamination of water with pollutants leached from these materials during the infiltration of atmospheric precipitation [16]. Due to the presence of organic micro-pollutants in the sludge [17] and contaminated soils [18], it is important to recognize the mobility of these compounds in the case of natural use resulting in the exposure to precipitation [19]. Previous co-authored research carried out under dynamic conditions reflecting the storage of sludge and PAHs washout showed that although these compounds are poorly water-soluble, the concentrations of these compounds in the extracts were relatively high [20].

Table 1
Limit values of organic micropollutants in proposal of Sludge Directive 86/278/EWG [14,15]

| Compounds | Limit concentration |
|---|---|
| Total of 11 PAHs, mg/kg d m | 6 |
| Total of 7 PCBs, mg/kg d m | 0.8 |
| AOX, mg/kg d m | 500 |
| PCDD/PCDF, ng/kg d m | 100 |
| DEHP, mg/kg d m | 100 |
| LAS, mg/kg d m | 2,600 |
| NPE, mg/kg d m | 50 |

AOX: Adsorbable organic halogens; DEHP: di(2-ethylhexyl) phthalates; PCDD/PCDDFs: polychlorinated dibenzodioxins/dibenzofurans; LAS: linear alkylbenzene sulphonates; NPE: nonylphenol and nonylphenol ethoxylate substances.]

The aim of this study was to assess the risk associated with the possibility of PAHs and PCBs leaching from sludge mixed with soils with different characteristics. The testing scope included:

- collection of biochemically stabilized sludge from a sewage treatment plant
- collection of soils from areas of diversified use
- determination of PAH and PCB concentration in sediments and soils
- extraction of PAHs and PCBs from sediments and soils by an aqueous extract method and determination of these micropollutants
- determination of PAH and PCB concentration in aqueous extracts from soil-sludge mixtures
- assessment of the risks arising from the application of sewage sludge to soils.

## 2. Materials and methods

### 2.1. Experimental

The tests were carried out in laboratory conditions using sludge stabilized in the process of aerobic stabilization. The sludge was collected from the sewage treatment plant in a daily amount of approximately 8,000 $m^3$/d. The sludge was mixed, centrifuged under laboratory conditions, and averaged samples were separated. The sludge was initially characterized by determining the hydration, dry matter content of organic compounds, and content of selected heavy metals [21]. Soils were collected from diverse areas including agricultural land and industrial land exposed to the anthropogenic pollution. The soils were initially characterized by performing determinations such as: reaction in

$H_2O$ and in KCl, sorption capacity, humidity, humus content and pH of the supernatant liquor.

Soil-sludge mixtures were prepared by adding sludge to soils in the amount of 5% by weight. The determined proportion corresponds to the legal conditions determining the possibility of introduction of the sludge into soils. To prepare aqueous extracts simulating the leaching of PAHs and PCBs under the influence of precipitation, the methodology of preparing an aqueous extract from solid materials specified in the Polish standard [22] was applied. This consisted in aqueous extraction of micro-pollutants from sludge, soils and mixtures of the two. For this purpose, the appropriate amount of tested materials was weighed and poured into distilled water until 1:10 ratio of dry mass to water volume was achieved. The mixtures were agitated for 4 h on a shaker and set aside for sedimentation, shaken again, decanted and extracted again with a new dose of water. The total contact time of the materials with water was 24 h. The determination of PAHs and PCBs in sludge, soils, mixtures and aqueous extracts prepared by procedure described above is presented in section 2.2.

### 2.2. Identification of PAHs and PCBs

The analysis of micropollutants was based on separation of these compounds from sludge samples by extraction, chromatographic separation of components and their qualitative and quantitative determination using a gas chromatograph coupled to a mass spectrometer (GC-MS). The extraction from sludge was carried out for 20 min in an ultrasonic bath with the addition of solvents. In the case of PAHs, a mixture of cyclohexane and dichloromethane was used for both solids (sludge, soil) and liquid samples (aqueous extracts). Separation of solvents from sludge/soil was carried out by centrifugation in a laboratory centrifuge. The extracts were then concentrated to a volume of 3 mL in a stream of nitrogen and purified under vacuum conditions. Extracts for the determination of PAH were purified on silica gel. A qualitative and quantitative analysis of PAHs was carried out using the GC-MS system. In the extracts from sludge and soils, and in aqueous extracts, the following PAHs were quantified:

- 3-ring; acenaphthene (Ac), phenanthrene (Fen), and fluorene (Fl)
- 4-ring; pyrene (Pir), fluoranthene (Flu)
- 5-ring; benzo (k)fluoranthene (BkF), benzo (b)fluoranthene (BbF), benzo (a)pyrene (BaP)
- 6-ring; benzo(ghi)perylene (Bper) and ideno(1,2,3–cd) pyrene (IndP).

In the case of PCB determination, liquid-solid or liquid-liquid extraction was carried out using 2-propanol. C18 octadecyl bed was used to separate the fraction containing PCBs. The purified extracts were concentrated again in a stream of nitrogen to a volume of 1 mL and then analysed using chromatogram. A system consisting of a capillary gas chromatograph and a mass spectrometer was used. The following 7 PCB congeners were identified: PCB 28, PCB 52, PCB 101, PCB 118, PCB 138, PCB 153, PCB 180 [23,24].

### 2.3. The risk assessment

The aim of the research is to analyze and assess the risk associated with the possibility of leaching PAHs and PCBs. Risk is defined as the probability of undesirable events, the occurrence of which causes negative effects on human health or life, the environment, or the economy. In the analyzed case, the risk analysis consists of identifying threats (micropollutants) and to assess the potential probability of their leaching from sediments and soils. The potential risk assessment identified the possible negative effects of these hazards on the environment and subsequently as a threat to food safety. For the purposes of risk assessment, the so-called acceptable contamination level (ACL) has been defined. The ACL was established based on guidelines, standards, and expert opinions [25–29]. For this purpose, current normative values, own research and literature data were analyzed.

In the statistical analysis of actual pollutant measurements, the average value of the measurements and the standard deviation are most frequently used. For the purposes of risk assessment, an upward deviation, i.e., the so-called semi-standard deviation, is calculated. Additionally, it was proposed to use the so-called coefficient of variation υ, which is defined as the relative standard deviation, described by Eq. (1) [26]:

$$\upsilon = \frac{\sigma_S}{x_a}$$

Where $x_a$ - average value, $s_s$ - semi-standard deviation

The coefficient of variation can be expressed as percentage. The larger the coefficient of variation, the higher the interchangeability class (diversity in the sample). Thus, the uncertainty in assessing individual parameters increases. A five-level risk scale was adopted to assess risk, i.e., negligible (NE), tolerable (TE), controlled (CO), intolerable (NT), and unacceptable (NA), and the following set of rules was defined:

- If $x_a$ £ ACL and υ < 20% then risk is negligible (NE)
- If $x_a$ £ ACL and υ = < 20–100% then risk is tolerated (TO)
- If $x_a$ £ ACL and υ > 100% then risk is controlled (CO)
- If $x_a^3$ 1 ×ACL < 2 ×ACL and υ = < 0–20% then risk is controlled (CO
- If $x_a^3$ 1 ×ACL < 2 ×ACL and υ = < 20–100% then risk is controlled (CO)
- If $x_a$ ³ 1 ×ACL < 2 ×ACL and υ > 100% then risk is not tolerated (NT)
- If $x_a^3$ 2 ×ACL and υ = < 0–20% then risk is not tolerated (NT)
- If $x_a^3$ 2 ×ACL and υ = < 20–100% then risk is not tolerated (NT)
- If $x_a^3$ 2 ×ACL and υ > 100 % then risk is not accepted (NA)

The risk assessment procedure is shown in Fig 1.

## 3. Results

### 3.1. General characteristics of sewage sludge and soils

The characteristics of the selected indicators of the tested sludge are presented in Tables 2 and 3.

Sewage sludge was characterized by 48% content of organic mass, which confirms the partial decomposition of organic compounds that takes place during the aerobic stabilization process. After the dewatering process, the dry matter content was 22%, standard value for sewage treatment plants. The pH of the supernatant liquor is also within the limits determined for other sludges. The content of heavy metals did not exceed the limit values set out in the current legal provisions regarding the use of municipal sludge in agriculture and in land remediation for agricultural purposes [1].

The values of the determined soil quality indicators are presented in Table 4.

The collected soils were diverse in terms of granulometry and quality. Soil 1 taken from an area used for agriculture was classified as loamy sand, while soil 2 from the industrial area was classified as weak loamy sand [30]. Soils differed in humus content and sorption capacity (including hydrolytic acidity and the amount of basic cations). Soil 1 is light, acidic soil with a relatively low sorption capacity. Soil 2 was characterized by sorption capacity that was almost double of that of Soil 1. The pH and humidity values were at the same level. The content of heavy metals did not exceed the limit values specified for fertilization with sewage sludge.

### 3.2. PAH concentrations in sludge, soils, and in aqueous extracts

Values of PAH concentrations in sludge, soils, and aqueous extracts are presented in Table 5. The concentration of the hydrocarbons tested was lower than the values determined for other sewage sludges [31], and the total average concentration of 10 compounds was 634 μg/kg. The sum of 16 PAHs in the sludge from five wastewater treatment plants in India reached 20.67 ± 4.14 mg/kg dry mass. Lower concentrations occur in sludges from treatment plants from European countries [14]. The average content of PAH in soils was 341 and 1,624 μg/kg dry mass respectively and was within the range reported by other authors for soils with different degrees of contamination [32]. In aqueous extracts from the tested materials, PAH concentrations were the highest in the case of sewage sludge.

The total concentration was comparable to the concentration of PAH from thermally processed sludge (17.5 μg/L) [33]. PAHs were extracted from agricultural soils, but in most cases the concentrations did not exceed 1 μg/L. The total concentration of PAHs in aqueous extracts from contaminated soils was approximately 10 times higher [34]. The determined values of PAH concentrations in mixtures of soils with sludge and in aqueous extracts are presented in Table 6.

Due to the addition of sewage sludge to soils, there was a slight (3–8%) increase in the content of PAH in the sludge-soil mixtures. The concentration in aqueous extracts from the uncontaminated soil mixture increased approximately by 200%. Therefore, the addition of sludge to this soil was significant and poses a risk of water pollution by increasing the concentrations in infiltrating precipitation. In the case of contaminated soil, the total PAH content increased by 43% after the introduction of sludge as the content of PAH in the sludge was lower than in the soil. Fig. 2 shows the changes in the total PAH content in sludge. soils and mixtures of the two; while Fig. 3 shows changes in the concentration of PAH in extracts after applying sludge to soils.

### 3.3. Concentrations of PCBs in sludge, soils and in aqueous extracts

The determined values of PCB concentrations in sludge, soils and aqueous extracts are presented in Table 7. The content of seven PCB congeners in the sludge did not

Table 2
Characteristics of stabilized sewage sludge after dewatering process

| | |
|---|---|
| Humidity, % | 78 |
| Dry mass, g/L | 228 |
| Organic substances, % dry mass | 48 |
| pH of supernatants | 8.2 |

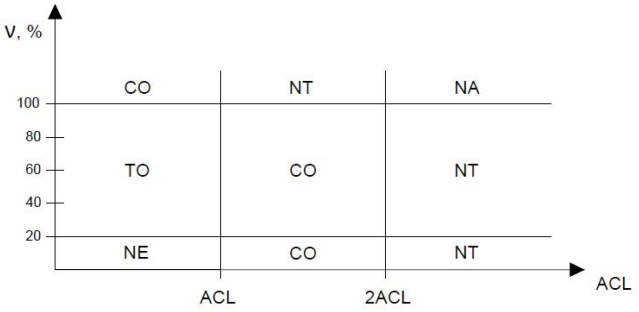


Fig. 1. The risk assessment procedure.

Table 3
The content of heavy metals both in sewage sludge, soils and limited value of this compounds in these materials

| Sewage sludge | Pb | Cd | Ni | Zn | Cu | Cr |
|---|---|---|---|---|---|---|
| | mg/kg d m | | | | | |
| Dewatered sewage sludge | 223 | 12.2 | 176 | 1,800 | 290 | 126 |
| Limited value of metals in sewage sludge [1] | 750 | 20.0 | 300 | 2,500 | 1,000 | 500 |
| Soil 1 | 8 | 0.3 | 11 | 56 | 17 | 22 |
| Soil 2 | 28 | 0.8 | 17 | 74 | 21 | 39 |
| Limited value of metals in soil [1] | 40 | 1.0 | 20 | 80 | 25 | 50 |

exceed 3.9 μg/kg dry mass. Concentrations of these compounds were within the limits obtained by other authors [35,36]. The content of PCBs in soils ranged from 0.6 to 1.7 μg/kg d mass. The concentrations of PCBs in aqueous extracts were small and did not exceed 0.8 μg/L in sewage sludge extract, and 0.2 μg/L in soil extracts. Due to the toxicity of these compounds, it should be concluded that their occurrence in the extracts poses a risk of contamination of waters during the infiltration of rainwater.

Values of PCB concentrations in sludge-soil mixtures and in aqueous extracts are presented in Table 8.

Fig. 4 and 5 shows changes in the total PCBs content in sludge, soils, mixtures of the two, and extracts from these materials, respectively.

Table 4
Characteristic of soils

| Soil | 1 Loamy sand | 2 Weak loamy sand |
|---|---|---|
| Humus content, % | 3.7 | 7.6 |
| Hydrolytic acidity | 3.9 | 4.9 |
| Sum of basic cations m.e./100 g | 1.5 | 4.1 |
| Sorption capacity | 5.4 | 9.0 |
| pH in KCl | 4.2 | 4.5 |
| pH in $H_2O$ | 4.8 | 5.2 |
| Humidity, % | 24 | 26 |

### 3.4. Risk assessment

The assessment of the potential risk associated with the possibility of leaching pollutants requires, in the first stage of research, the definition of the so-called acceptable contamination level (ACL), which was adopted based on legal acts or

Table 5
PAHs concentration both in sewage sludge, soils and in aqueous extracts from these materials

| PAHs | PAHs concentration μg/kg d m | | | PAHs concentration in aqueous extracts from materials μg/L | | |
|---|---|---|---|---|---|---|
| | Sewage sludge | Soil 1 | Soil 2 | Sewage sludge | Soil 1 | Soil 2 |
| Acenaphtene | 51.2 ± 4.3 | 47.2 ± 3.5 | 37.4 ± 3.8 | 3.31 ± 0.15 | 1.04 ± 0.11 | 6.32 ± 0.32 |
| Fluorene | 57.1 ± 4.8 | 34.5 ± 4.6 | 52.8 ± 7.4 | 4.1 ± 0.31 | 0.78 ± 0.22 | 6.25 ± 0.32 |
| Phenanthrene | 53.0 ± 3.8 | 39.0 ± 3.5 | 60.5 ± 4.7 | 1.24 ± 0.32 | 0.87 ± 0.14 | 4.85 ± 0.25 |
| Fluoranthene | 77.0 ± 5.5 | 32.8 ± 5.1 | 184.8 ± 8.1 | 1.58 ± 0.23 | 1.11 ± 0.13 | 4.65 ± 0.24 |
| Pyrene | 67.0 ± 6.5 | 26.8 ± 4.8 | 137.5 ± 8.4 | 1.24 ± 0.24 | 0.85 ± 0.11 | 3.98 ± 0.26 |
| Benzo(b)fluoranthene | 63.0 ± 4.5 | 33.4 ± 4.1 | 231.7 ± 5.3 | 1.08 ± 0.23 | 0.42 ± 0.11 | 4.74 ± 0.34 |
| Benzo(k)fluoranthene | 63.2 ± 5.8 | 41.0 ± 3.1 | 250.8 ± 6.6 | 1.11 ± 0.17 | 0.36 ± 0.13 | 4.52 ± 0.23 |
| Benzo(a)pyrene | 59.0 ± 7.5 | 27.7 ± 2.4 | 176.3 ± 2.5 | 1.35 ± 0.16 | 0.28 ± 0.21 | 3.65 ± 0.23 |
| Benzo(g.h.i) perylene | 69.2 ± 8.4 | 34.7 ± 7.1 | 293.7 ± 5.1 | 1.35 ± 0.21 | 0.13 ± 0.12 | 3.98 ± 0.26 |
| Indeno(1.2.3c.d)pyrene | 75.0 ± 3.5 | 24.2 ± 2.2 | 199.1 ± 4.2 | 1.69 ± 0.21 | 0.15 ± 0.11 | 3.65 ± 0.23 |

Table 6
PAHs concentration both in mixtures of soils with sewage sludge and in aqueous extracts

| PAHs | PAHs concentration in mixture of soils with sewage sludge μg/kg d m | | AHs concentration in aqueous extracts from mixtures μg/L | |
|---|---|---|---|---|
| | Soil 1 + sewage sludge | Soil 2 + sewage sludge | Soil 1 + sewage sludge | Soil 2 + sewage sludge |
| Acenaphtene | 49.0 ± 2.6 | 49.2 ± 4.8 | 2.68 ± 0.22 | 9.14 ± 0.75 |
| Fluorene | 36.9 ± 8.2 | 73.0 ± 1.6 | 2.55 ± 0.22 | 8.04 ± 0.83 |
| Phenanthrene | 48.0 ± 2.3 | 81.0 ± 3.6 | 1.85 ± 0.21 | 7.05 ± 0.05 |
| Fluorantene | 36.9 ± 7.2 | 185.2 ± 14.2 | 1.22 ± 0.04 | 7.68 ± 0.06 |
| Pyrene | 42.0 ± 3.9 | 139.2 ± 9.4 | 1.93 ± 0.05 | 5.14 ± 0.04 |
| Benzo(b)fluoranthene | 36.0 ± 8.1 | 232.0 ± 16.7 | 1.54 ± 0.06 | 5.12 ± 0.06 |
| Benzo(k)fluoranthene | 44.0 ± 6.2 | 252.1 ± 14.8 | 1.56 ± 0.04 | 5.88 ± 0.04 |
| Benzo(a)pyrene | 39.3 ± 5.3 | 178.0 ± 12.8 | 1.47 ± 0.04 | 5.96 ± 0.11 |
| Benzo(ghi)perylene | 36.4 ± 9.1 | 277.1 ± 8.4 | 1.68 ± 0.12 | 5.06 ± 0.06 |
| Indeno(1.2.3c.d)pyrene | 37.0 ± 4.5 | 202.1 ± 6.8 | 1.54 ± 0.11 | 6.88 ± 0.05 |

Table 7
PCBs concentration both in sewage sludge, soils and in aqueous extracts from these materials

| PCBs congeners | PCBs concentration μg/kg d m | | | PCBs concentration in aqueous extracts from materials μg/L | | |
|---|---|---|---|---|---|---|
| | Sewage sludge | Soil 1 | Soil 2 | Sewage sludge | Soil 1 | Soil 2 |
| PCB 28 | 0.12 ± 0.01 | 0.01 ± 0 | 0.13 ± 0.01 | 0.03 ± 0.01 | 0.01 ± 0.005 | 0.03 ± 0 |
| PCB 52 | 0.88 ± 0.02 | 0.02 ± 0.01 | 0.21 ± 0.03 | 0.07 ± 0.02 | 0.01 ± 0 | 0.02 ± 0 |
| PCB 101 | 0.65 ± 0.02 | n.o | 0.34 ± 0.03 | 0.06 ± 0.02 | n.o | 0.02 ± 0 |
| PCB 118 | 0.37 ± 0.01 | 0.15 ± 0.01 | 0.22 ± 0.03 | 0.14 ± 0.02 | n.o | 0.03 ± 0.01 |
| PCB 138 | 0.26 ± 0.01 | 0.11 ± 0.01 | 0.19 ± 0.02 | 0.09 ± 0.02 | n.o | 0.01 ± 0 |
| PCB 153 | 1.17 ± 0.03 | 0.16 ± 0.02 | 0.32 ± 0.03 | 0.26 ± 0.02 | 0.01 ± 0 | 0.02 ± 0 |
| PCB 180 | 0.41 ± 0.02 | 0.12 ± 0.01 | 0.22 ± 0.01 | 0.18 ± 0.02 | 0.01 ± 0 | 0.04 ± 0.01 |

n.o. – no detected

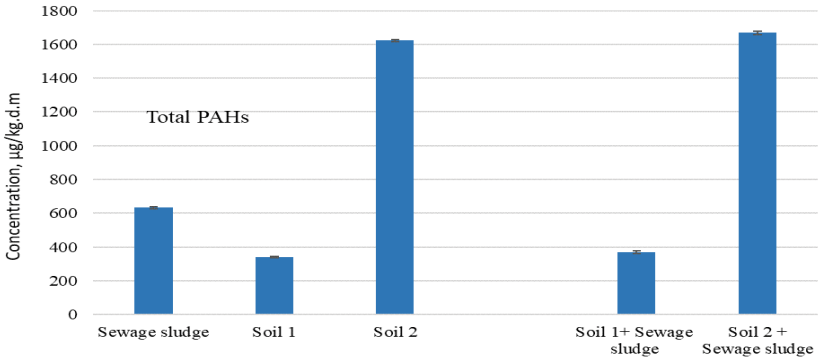


Fig. 2 Changes in the total PAHs concentration both in sewage sludge, soils and mixture of these materials.

Table 8
PCBs concentration both in mixtures of soils with sewage sludge and in aqueous extracts

| PCBs congeners | PCBs concentration in mixture of soils with sewages sludge μg/kg s m | | PCBs concentration in aqueous extracts from mixtures μg/L | |
|---|---|---|---|---|
| | Soil 2 + sewage sludge | Soil 1 + sewage sludge | Soil 2 + sewage sludge | Soil 2 + sewage sludge |
| PCB 28 | 0.01 ± 0.005 | 0.13 ± 0.02 | 0.01 ± 0 | 0.04 ± 0.01 |
| PCB 52 | 0.02 ± 0.05 | 0.21 ± 0.02 | 0.01 ± 0 | 0.02 ± 0.01 |
| PCB 101 | n.o | 0.34 ± 0.05 | 0.01 ± 0 | 0.03 ± 0.01 |
| PCB 118 | 0.15 ± 0.01 | 0.22 ± 0.04 | 0.01 ± 0 | 0.03 ± 0.01 |
| PCB 138 | 0.11 ± 0.02 | 0.19 ± 0.02 | 0.01 ± 0 | 0.02 ± 0.01 |
| PCB 153 | 0.16 ± 0.03 | 0.32 ± 0.03 | 0.01 ± 0 | 0.02 ± 0.01 |
| PCB 180 | 0.12 ± 0.04 | 0.22 ± 0.04 | 0.01 ± 0 | 0.05 ± 0.01 |

literature studies [37,38]. In terms of PAH and PCB content, the legal provisions are not complete; limit values are only proposed for sludge intended for agriculture (Table 1) in relation to soils and Polish legislation specifies threshold values for risk assessment (Table 9).

However, there are no limit values for the concentrations of these compounds in aqueous extracts. According to the currently applicable Polish provisions on the qualification of soil content, it is considered that PAHs and PCBs [37] should be included in the analysis of the risk of soil surface contamination. The permissible content of these substances in the soil is determined for a depth of 0–0.25 m and more than 0.25 m, considering different soils depending on the use and water permeability. Threshold values for PAH and PCB concentrations are presented in Table 10. As already stated, in the currently applicable legal acts there are no permissible concentrations in aqueous extracts from sludge, soils and mixtures of the two. Therefore, in this case, these values

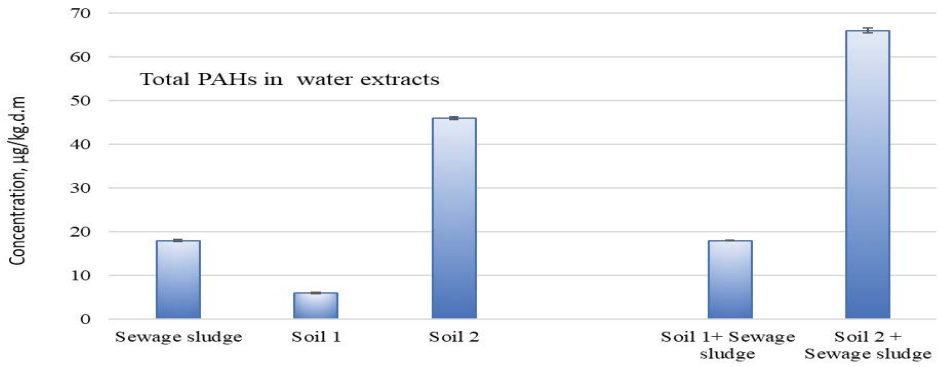


Fig. 3. Changes in the total PAHs concentration in extracts.

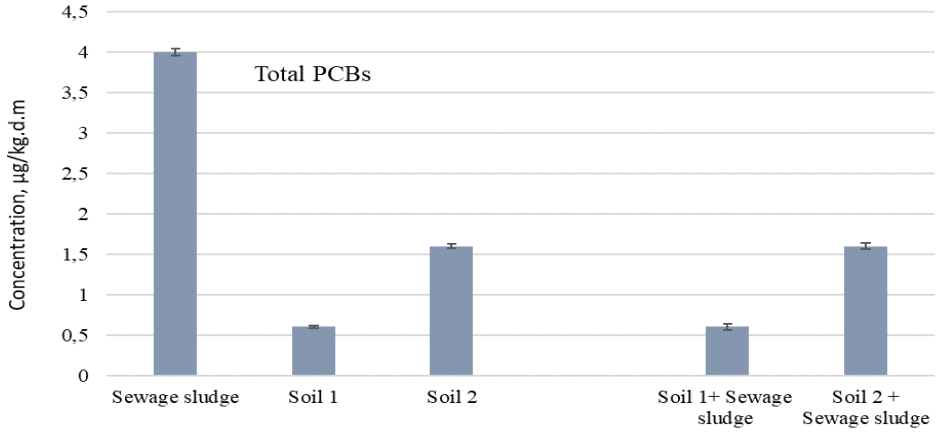


Fig. 4. Changes in the total PCBs concentration both in sewage sludge, soils and mixture of these materials.

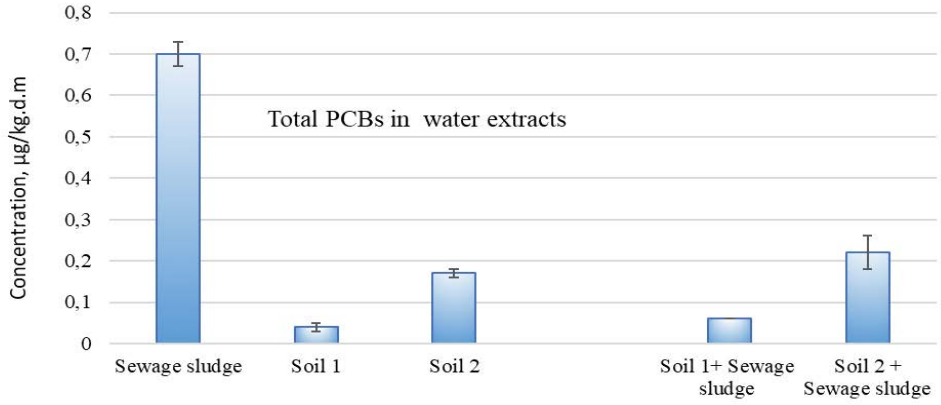


Fig. 5. Changes in the total PCBs concentration in extracts.

were determined based on the data related to the conditions that need to be met when discharging sewage into waters or into the ground, as well as when discharging rainwater or snowmelt into waters or into water facilities [38]. According to this provision, substances classified as particularly harmful to the aquatic environment and cause pollution to waters, should be eliminated, and are characterized by the durability in the environment, bio accumulative capacity, and a risk to waters and human life or health, include substances that have carcinogenic, mutagenic or teratogenic properties in the aquatic environment or through this environment. Therefore, since PAHs and PCBs show carcinogenicity, mutagenicity and are classified as persistent pollutants, it was assumed that the permissible concentration

Table 9
Limit value both of PAHs and PCBs contents in soils for risk assessment [ ]

| | PAHs/PCBs | 1–Soil groups for depth below 0.25 m | | | | Soil groups for depth over 0.25 m | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | I | II | III | IV | I | II | III | IV |
| | | μg/kg dry mass of soil | | | | μg/kg dry mass of soil | | | |
| 1 | Naphtalene | 100 | 100 | 1000 | 20000 | 5000 | 20000 | 10000 | 40000 |
| 2 | Anthracene | 200 | 200 | 1000 | 20000 | 5000 | 20000 | 10000 | 40 |
| 3 | Chrysene | 200 | 200 | 1,000 | 20,000 | 5,000 | 20,000 | 10,000 | 40 |
| 4 | Benzo(a) anthacene | 100 | 100 | 1,000 | 20,000 | 5,000 | 20,000 | 10,000 | 40 |
| 5 | Dibenzo(ah)anthracene | 100 | 100 | 1,000 | 20,000 | 5,000 | 20,000 | 5,000 | 20 |
| 6 | Benzo(a) pyrene | 100 | 100 | 1,000 | 20,000 | 5,000 | 20,000 | 5,000 | 40 |
| 7 | Benzo(b) fluoranthene | 100 | 100 | 1,000 | 20,000 | 5,000 | 20,000 | 5,000 | 20 |
| 8 | Benzo(k) fluoranthene | 100 | 100 | 1,000 | 20,000 | 5,000 | 20,000 | 5,000 | 20 |
| 9 | Benzo(ghi) perylene | 200 | 200 | 1,000 | 20,000 | 5,000 | 20,000 | 5,000 | 100 |
| 10 | Indeno(1.2.3c.d) pyrene | 200 | 200 | 1,000 | 20,000 | 5,000 | 20,000 | 5,000 | 20 |
| | Sum of 10 PAHs | 1,400 | 1,400 | 10,000 | 200,000 | 500,000 | | | |
| | Carcinogenic PAHs No. 3–10 | 1,100 | 1,100 | 800 | | | | | |
| | PCBs Congeners: PCB 28. PCB 52. PCB 101. PCB118. PCB 138. PCB 153. PCB 180 | 20 | 20 | 20 | 2,000 | 100 | 2,000 | 500 | 5,000 |

for PCBs will be 0, and for PAHs - it was determined to be 2 μg/L, based on previous co-authored studies and previous provisions on the conditions of introduction of treated sewage into the aquatic environment (into water or into the ground). Only one compound representing the PAH group was included in the repealed Regulation (currently not in force). It was BaP, permissible concentration of which in the sewage discharged to the receivers was 2 μg/L [39]. Based on the data presented in Table 7 and in accordance with the justification above, the ACL Criteria for PAHs and PCBs were adopted. Then, based on the tests concerning the content of individual pollutants, i.e., the average value and the semi standard deviation, the coefficients of variation were determined. This allowed for a risk assessment, which was carried out in accordance with the procedure presented in Fig. 1. The results are presented in Tables 10 and 11.

For PAHs and PCBs tested in sediments and soils, the risk is negligible. It should be noted that in this case, both the content of PAHs and the coefficients of variation are at levels much lower than the adopted criteria values. For water extracts, the risk is at the intolerable level, mainly due to exceeding the criteria values; additionally, for soil 1, the value of the coefficient exceeds 20%, which proves the average variability of values in the tested sample.

For PAHs tested in soil-sediment mixtures, the risk is negligible for soil 1 and controlled for soil 2. For water extracts, the risk is at an intolerable level, mainly due to exceeding the criteria values. For the tested PCBs tested in soil-sediment mixtures, the risk is negligible. For water extracts, the risk is at an intolerable level, mainly due to exceeding the criteria values. The coefficients of variation in each case are below 20%, proving the low variability of the values in the tested samples.

## 4. Summary and conclusions

The content of PAH in sludge and soils does not exceed the limits determined by other authors and previous co-authored research. The content of determined PAHs in the tested soils did not exceed the limit values for 10 compounds and for soil groups:

- in soil 1 (341 μg/kg dry mass) PAH content did not exceed the value of 1,400 μg/kg dry mass specified for soils of groups I and II,
- in soil 2 (1,624 μg/kg dry mass) PAH content exceeded the values for group I and II soils but is lower than the permissible values for soils of group III (10,000 μg/kg dry mass)

Sewage sludge was also contaminated by PAH (634 μg/kg dry mass), but the proposed limit value for the sludge for environmental use (6,000 μg/kg dry mass) was not exceeded. Therefore, considering the PAH content, this sludge could be introduced into the soil. In this case, the content would increase by 28 μg/kg dry mass or 44 μg/kg dry mass for soils 1 and 2, respectively.

The limit content of PAHs in soils of groups I and II should be less than 1,400 μg/kg dry mass. Therefore, sludge should not be introduced into soils, especially soil 2, in case of which an already increased initial PAHs content was noted. Studies of PAH leaching from sewage sludge and soil showed that these compounds migrated to infiltrating water, but their concentrations were varied. PAHs are relatively poorly soluble in water but exhibit an affinity for particulate matter and are classified as readily adsorbable on slurry particles forming sewage sludge released from

Table 10
Risk assessment of PAHs and PCBs in tested materials

| PAHs | Sum of PAHs μg/kg s m | | | Sum of PAHs in aqueous extracts μg/L | | |
|---|---|---|---|---|---|---|
| | Sewage sludge Sum of 11 PAHs | Soil 1 - Sum of 10 PAHs | Soil 12 - Sum of 10 PAHs | Sewage sludge | Soil 1 | Soil 2 |
| Average value | 634.7 | 341.3 | 1,624.6 | 18.05 | 5.99 | 46.59 |
| Semi-standard deviation | 5.3 | 4.8 | 6.1 | 0.22 | 0.16 | 0.26 |
| Coefficient of variation | 0.84 | 1.41 | 0.38 | 1.22 | 2.67 | 0.56 |
| ACL | 6,000 (limit value for sewage sludge) | 1,400 (limit value for I and II group of soil) | 10,000 (limit value for III group of soil) | 2 | 2 | 2 |
| Risk assessments | NE | NE | NE | NT | NT | NT |
| | Sum of 7 PCB μg/kg d m | | | Sum of 7 PCBs μg/kg d min aqueous extracts | | |
| | Sewage sludge | Soil 1 | Soil 2 | Sewage sludge | Soil 1 | Soil 2 |
| Average value | 3.86 | 0.57 | 1.63 | 0.73 | 0.04 | 0.17 |
| Semi-standard deviation | 0.04 | 0.02 | 0.03 | 0.03 | 0.01 | 0.01 |
| Coefficient of variation | 1.03 | 3.5 | 1.8 | 4.11 | 25 | 5.88 |
| ACL | 800 (limit value for sewage sludge) | 20 (limit value for I and II group of soil) | 20 ((limit value for I and II group of soil) | 0 | 0 | 0 |
| Risk assessment | NE | NE | NE | NT | NT | NT |

NE – negligible, NT - not tolerated

Table 11
Risk assessment of PAHs and PCBs in mixtures of soil with sewage sludge and in aqueous extracts

| PAHs | Sum of PAHs μg/kg d m | | Sum of PAHs in aqueous extracts μg/L | |
|---|---|---|---|---|
| | Soil 1 + sewage sludge | Soil 2 + sewage sludge | Soil1 + sewage sludge | Soil 2 + sewage sludge |
| Average value | 369.5 | 1,668.9 | 18.02 | 65.95 |
| Semi-standard deviation | 6.4 | 9.8 | 0.13 | 0.51 |
| Coefficient of variation | 1.7 | 0.6 | 0.72 | 0.77 |
| ACL | 1,400 (limit value for I and II group of soil) | 1,400 (limit value for I and II group of soil) | 2 | 2 |
| Risk assessment | NE | CO | NT | NT |
| PCBs | Sum of 7 PCBs μg/kg d m | | Sum of 7 PCBs in aqueous extracts μg/L | |
| | Soil1 + sewage sludge | Soil 2 + sewage sludge | Soil1 + sewage sludge | Soil 2 + sewage sludge |
| Average value | 0.58 | 1.65 | 0.06 | 0.22 |
| Semi-standard deviation | 0.04 | 0.04 | 0 | 0.04 |
| Coefficient of variation | 1.7 | 0.6 | 0.72 | 0.77 |
| ACL | 20(graniczna dla I i II grupy gleb) | 20(graniczna dla I i II grupy gleb) | 0 | 0 |
| Risk assessment | NE | NE | NT | NT |

NE – negligible, NT - not tolerated, CO – controlled

sewage during their treatment. The octanol/water partition coefficient for the test compounds is less than 6.8, and the solubility of PAH in water is in the range of 0.0005 to 3.93 mg/L, except for naphthalene, solubility of which is 31.7 mg/L. Therefore, the concentrations of naphthalene in aqueous extracts were several times higher than those of other hydrocarbons. The solubility of PCBs in water is two orders of magnitude lower than the solubility of PAHs

(0.3–24 μg/L). Therefore, during intensive shaking with water, PAHs and PCBs were most likely adsorbed on micro suspensions and were elevated to the aqueous phase during extraction. Chen et al. [33] claim that PAH leaching may also be associated with the release of hydrophobic organic compounds that form a mobile phase facilitating PAH mobilization into water. The leaching of PAHs may also be associated with the release of certain metals ions (e.g. calcium or aluminium).

The total concentration of PAH in aqueous extracts from unfertilized soils was 5.99 and 46.59 μg/L. The introduction of sludge into the soil resulted in an increase in the concentration of PAH in aqueous extracts by 12 or 20 μg/L. Therefore, sludge meeting the legal requirements introduced into both contaminated and non-contaminated soil cause an increase in the amount of PAH leaching, creates a risk of contamination of the aquatic environment. For PCBs, the total content of these compounds is 0.6 or 1.63 μg/L and the content of each of the congeners determined does not exceed the limit values for group I soils specified to be 20. In aqueous soil extracts, the concentrations of PCBs are less than 0.2 μg/L, but PCBs are not expected to be present in extracts from soils, sludge, or mixtures of the two materials.

In the risk analysis, an original approach based on the assessment of two criteria, i.e., the acceptable level of pollution and the coefficient of variation, was proposed as the assessment criterion. This approach includes a comparison of the measured value with the adopted acceptable level (ACL) and a differentiated analysis (variability) of the measured values (degree of homogeneity of the tested sample). In qualitative risk analysis, such an approach is justified due to the need to take into account the diversity of measurements resulting from changing external conditions and factors reflecting the diversity and specificity of micropollutants. The greater the coefficient of variation, the more significant the heterogeneity of the test sample, and the greater the uncertainty coefficient. The adopted method can be used in quality risk analyzes, and the adopted criteria values can be modified and adapted to specific micropollutants and the conditions of their occurrence.

**Acknowledgements:**

The work of the corporation under both the statutory subsidy of the Czestochowa University of Technology and Rzeszow University of Technology

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