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Occurrence of heavy metals and PAHs in soil and plants after application of sewage sludge to soil

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ABSTRACT

The results of investigations on heavy metals and polycyclic aromatic hydrocarbons (PAHs) content in mixed soil fertilized with sewage sludge are presented. The concentration of these micropollutants in various parts of a basket willow *Salix viminalis* grown on this substratum was also analyzed. Aerobically stabilized, dewatered, and hygienized sewage sludge (a dose of 90 tons of dry matter per hectare) was used to fertilize the soil. *S. viminalis* was planted on the soil amended with sewage sludge. The samples for analyses were taken after five vegetatives; they were both soil samples and parts of plants (roots, stems, and leaves). The concentration of heavy metals and PAHs was analyzed in the samples. The concentration of heavy metals in soil after five seasons of fertilizing with sewage sludge was at most cases higher than defined in soil at the beginning of the experiment. The concentration of Cr in soil after five years of *S. viminalis* cultivation was, however, lower than at the outset. The average concentration of Cr in biomass of a basket willow equaled to 9.3 $mg/kg_{d.m.}$ and it was higher than the average content of this element in not fertilized soil samples (4.6 $mg/kg_{d.m.}$). The content of other heavy metals in willow biomass was lower than the soil concentration and was equal to 0.7, 7.9, 1.3, 13.2, and 47.0 $mg/kg_{d.m.}$ for Cd, Cu, Ni, Pb, and Zn, respectively. The concentration of 15 PAHs total in soil did not exceed 700 $\mu g/kg_{d.m.}$. The total concentration of 15 PAHs was also analyzed in particular parts of *S. viminalis*. The average total concentration of these micropollutants in roots was equal to 67 $\mu g/kg_{d.m.}$. The total concentration of 15 PAHs in above ground parts of plants was equal to 115 and 55 $\mu g/kg_{d.m.}$ for leaves and stems, respectively.

Keywords: Soil; Sewage sludge; *Salix viminalis*; Heavy metals; PAHs; HPLC-DAD

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1. Introduction

In 2011, the most commonly used method of sewage sludge management in Poland was its agricultural use; 116.2 thousand tons of sewage sludge dry matter was managed in this way. Some other important management methods used were land reclamation (for 54.4 thousand tons of sewage sludge d.m.) and cultivation of plants for the compost production (31.0 thousand tons of sewage sludge d.m.). Thermal stabilization was in the year 2011 used to utilize 8% of municipal sewage sludge; 51.4 thousand tons of sewage sludge d.m. was landfilled. According to the statistical data, about 41% (212.4 thousand tons of sewage sludge d.m.) of sewage sludge made up dumping in disposal sites, drying beds, and stabilization ponds at wastewater treatment plants [1] — Fig. 1.

Sewage sludge is a source of biogenic compounds as well as macro- and micropollutants which are necessary for plant growth. The agricultural use of sewage sludge is one of the most preferred methods of its management. It can also be used at plantations of energetic plants. The agricultural use of sewage sludge makes it possible to achieve ecosystem balance [2,3]. Both nutrients for plants and toxic compounds could be, however, introduced into the soil with sewage sludge. Main inorganic toxicants are heavy metals—cadmium, lead, mercury, zinc, and copper [4,5]. Organic toxicants are mainly polycyclic aromatic hydrocarbons (PAHs), halogen-derivatives, nonylphenols, phthalates, and surfactants [6–9]. According to Polish legislation, the application of sewage sludge in agriculture is limited by permissible heavy metals' (Zn, Pb, Cu, Cr, Hg, Ni, and Cd) concentrations and pathogens' (*Salmonella*, *Ascaris* sp., *Trichuris* sp., *Toxocara* sp.) presence [10]. Proposed changes in EU Directive demand the control of toxic organic micropollutants in sewage sludge applied in agriculture including PAHs, PCBs, PCDD/PCDF, DEHP, NPE, AOX, and LAS [11].

Until now, the correlation between concentration of heavy metals and PAHs present in sewage sludge applied into the soils has been rather rarely investigated. Among others, Lazzari et al. tried to assess the relationship between the concentration of PAHs and Hg, Cd, Zn, and Cu in composted sewage sludge [9]. Maliszewska-Kordybach et al. investigated the effects of Zn, Pb, and Cu on persistence of PAHs in soils amended with sewage sludge. The results of the investigation indicated that metals inhibited biodegradation of PAHs both in sewage sludge, soils, and mixtures of sludge and soil [12].

The use of sewage sludge at energetic plants plantations is one of the prevailing ways of sludge management. According to the results obtained by other authors, the changes in soil and plants properties were observed during exploitation of the plantations. The changes were observed mainly in concentrations of nutrients. Fates of toxic micropollutants (e.g. PAHs) usually are not monitored. The data on micropollutants concentrations in soil and plants of energetic plants plantations which are available in literature concern mainly the content of heavy metals and PAHs in soil, sewage sludge, and parts of plants. The results are mainly collected in small experimental plots at early stages of plantation exploitation. The correlation between PAHs content in plants and in soil was confirmed [13–18]. The results are, however, not clear-cut. It was proved that plants could metabolize these ksenobiotics via oxidation and co-metabolism. By-products of the reactions can be cumulated in plant

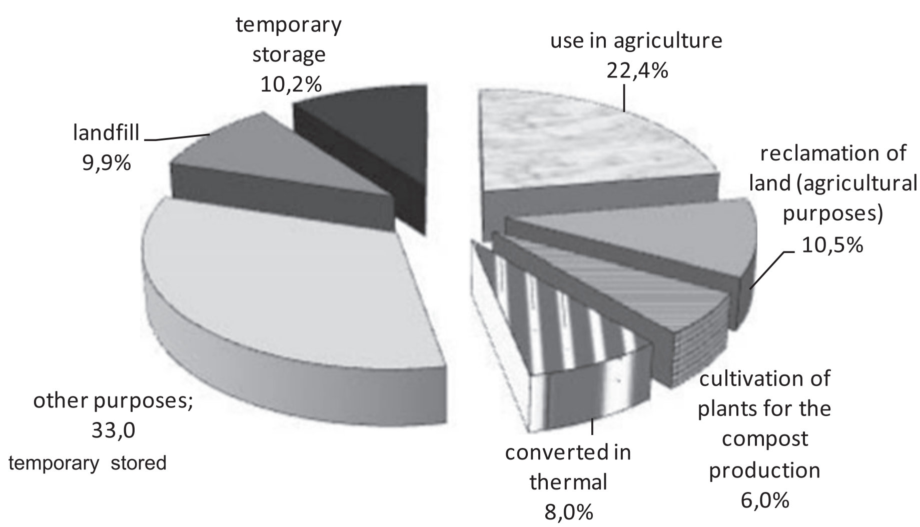

Fig. 1. Percent share of various sewage sludge management methods in Poland in 2011.

tissues, e.g. roots, stems, and leaves. Cumulation of these compounds in rhizosphere was also stated. As well as degradation of PAHs during phytoremediation in which cereals, grass, and vegetables were used [14,15,17,18]. Simultaneously, however, inhibition of germination and development of plants by PAHs was confirmed [16].

Taking into account the variability of literature data and the necessity to analyze the level of pollution of plants under technical scale, some investigation on the selected heavy metals' content and PAHs in soil fed with anaerobically stabilized sewage sludge as well as in selected parts of a basket willow was undertaken.

2. Materials and methods

2.1. Soil

Lands designated for basket willows plantation are located next to wastewater treatment plant in western Poland. The land was divided into experimental plots. The plots differed in properties of surface soil. Section A (area of research work) was managed in 2002.

Soil analysis undertaken before setting up the plantation proved that on this site mosaic of soils occurred; they were mainly grey–brown podzolic soils and brown soils, of quality classification IVa, IVb, V, and VI. The concentration of heavy metals in the surface layer of soil (up to 30 cm) taken from experimental plot was analyzed. The results of heavy metal content in the soil, as well as of the concentration of phosphorus and potassium are listed in Table 1.

Among heavy metals present in soil, zinc was observed in the highest concentration (37.24 mg/$kg_{d.m.}$). The concentration of lead was equal to 15.19 mg/$kg_{d.m.}$. Concentrations of heavy metals in soil indicated that according to the Polish legislation standards (Regulation of the Minister of Environment of 1 August 2002 concerning municipal sewage sludge) sewage sludge can be applied into the soil since the values did not exceed the ones set for land reclamation (but for nonagricultural purposes).

Table 1
Properties of the surface layer of soil before planting basket willow

Parameter	Value
pH_{KCl}	6.70
P_2O_5, mg/100$g_{d.m.}$	27.30
K_2O, mg/100$g_{d.m.}$	7.90
Lead, mg/100$g_{d.m.}$	15.19
Cadmium, mg/100$g_{d.m.}$	0.12
Chromium, mg/100$g_{d.m.}$	5.25
Copper, mg/100$g_{d.m.}$	5.36
Nickel, mg/100$g_{d.m.}$	3.20
Mercury, mg/100$g_{d.m.}$	0.043
Zinc, mg/100$g_{d.m.}$	37.24

2.2. Sewage sludge

Sewage sludge was taken from a municipal wastewater treatment plant located in western Poland. It is mechanical–biological WWTP (Fig. 2). The first stage of the treatment is screening on slotted screens Rotopas type. Afterwards they go into an aerated grit chamber. Then wastewater passes into a biological sector. Bioreactors consist of two rings—the external one is an activated sludge chamber (it works as a biological ditch), the internal one is a secondary clarifier. Simultaneous nitrification and denitrification occur in an activated sludge chamber. Phosphorus is removed chemically by simultaneous precipitation. Sewage sludge is aerobically stabilized. Stabilized sludge is dewatered at filter presses (the process is supported by Fe salts and lime addition). Dewatered and hygienized sludge is used as a fertilizer in the plantation of a basket willow.

Physicochemical properties of the sludge (Table 2) proved that they were epidemically safe and contained permissible concentrations of heavy metals. Due to that they could be used in agriculture and for land reclamation [10].

When comparing the values of heavy metal concentration in sewage sludge and in soil with Polish legislation standards, one could state that the main contaminant which restricts the agricultural use of the waste material used during the experiment was zinc. Besides, the copper concentration was at a relatively high level. Concentrations of other metals indicate that they were not limiting compounds in the case of agricultural use.

2.3. Experimental procedure

Properties of sewage sludge from WWTP (Table 2) indicated its mileage as a fertilizer. Alkalinity level made it possible to increase doses of sewage sludge. Simultaneously, optimal characteristics of substratum could be achieved, making certain perennial growth of the basket willow. The dose of sewage sludge was equal to 90 tons of d.m. per hectare (which reached 45% of maximum sludge dose allowed in the case of an agricultural use of the land) [19].

The willow was planted at an experimental plot in 2002. Plantings of tree stocking were equal to 33,400 seedlings per hectare. To set the plantation 40 seedlings of osier were used (of Nordic strain, clones Ulv, and York).

Table 2
Selected physicochemical properties of sewage sludge from WWTP in 2002

Parameter	Average value
pH	11.25
Humidity, %	81.31
Dry matter, %	18.69
Organic dry matter, %d.m.	34.22
Total nitrogen, %d.m.	2.79
Total phosphorus, %d.m.	0.8
Calcium, %d.m.	5.23
Magnesium, %d.m.	0.92
Lead, mg/kg d.m.	102
Cadmium, mg/kg d.m.	1
Mercury, mg/kg d.m.	0
Nickel, mg/kg d.m.	29
Zinc, mg/kg d.m.	1,050
Copper, mg/kg d.m.	136
Chromium, mg/kg d.m.	28
Pathogenic bacteria genus *Salmonella* in 100 g of sludge	Not isolated
Living eggs of worms *Ascaris* sp., *Trichuris*, pieces/kg d.m.	Not detected

Lands for plantation were managed at early spring and involved the following steps:

- supply of hygienic and dewatered sewage sludge into an experimental plot (Fig. 3),
- surfacing the determined dose of sludge onto the plot surface (Fig. 4),
- planting of basket willow seedlings.

2.4. Analytical methods

Samples of mixture soil and sewage sludge as well as parts of plants were collected in summer after 5 years of exploitation of that experimental plot. Egner stick was used to collect samples of soil and sewage sludge mixture. The samples were taken from the depth of 0–30 cm; 25 individual samples were taken once from points regularly disposed on an experimental plot area. All samples which were taken from the plot were mixed to obtain representative samples. Air-dried samples were sieved through a sieve with mesh diameter of 1 mm. In the samples, prepared as described above (in fine fraction), selected heavy metals and 16 PAHs were analyzed.

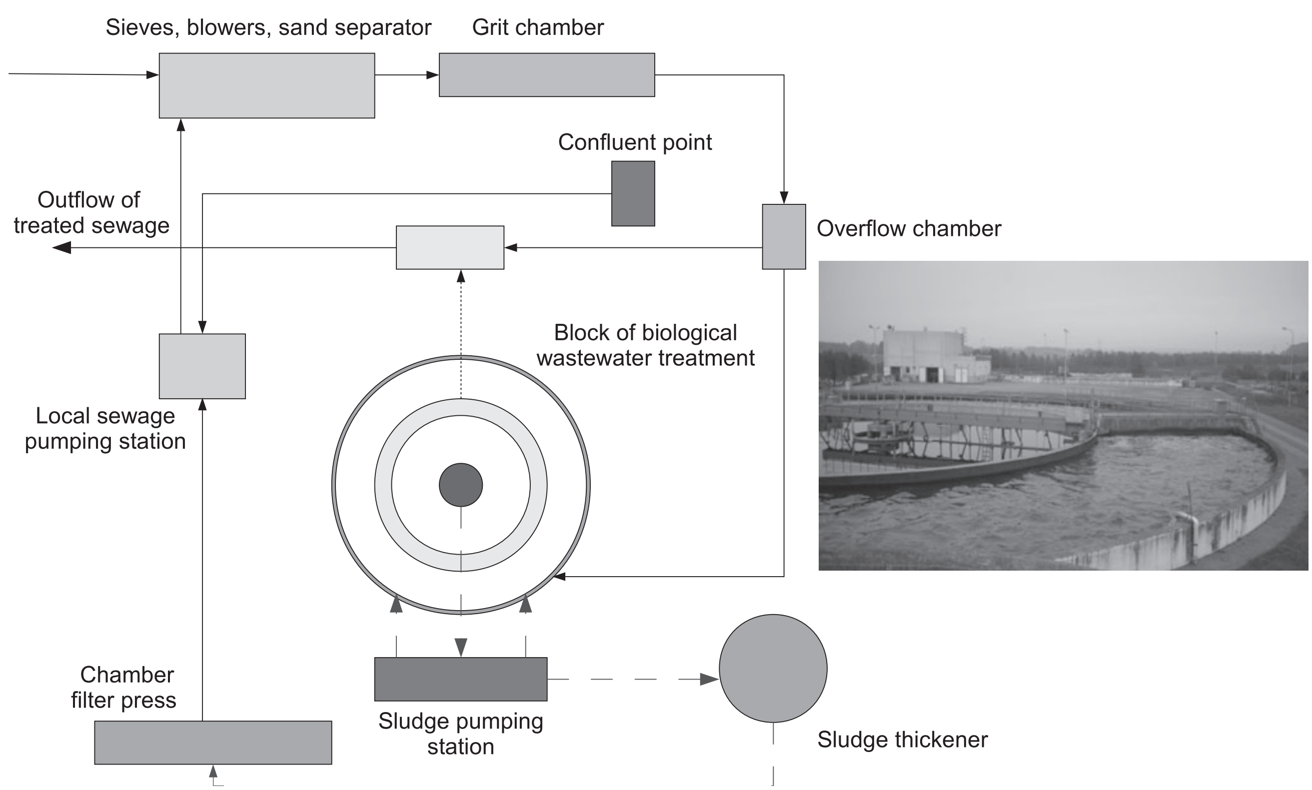

Fig. 2. Diagram flow and view of biological treatment unit of WWTP.

Fig. 3. Sewage sludge tip before its surfacing onto experimental plot.

Fig. 4. Experimental plot with surfaced sewage sludge.

To collect part of plants whole, healthy plants were dug. Roots were carefully cleaned to remove soil. Plants were divided into roots, stems, and leaves. Leaves were collected by picking several leaves with petioles at the height of about half of the willow corona. Stems were taken from a half of three heights. Roots samples were of 20 cm length. Plant samples were left in a canopied chamber at room temperature to dry. Air-dried parts of plants (roots and stems) were mechanically ground to obtain wood chips. Leaves were ground in a mortar. In the samples, prepared as described above, heavy metals and 16 PAHs were analyzed.

To analyze selected heavy metals (lead, cadmium, chromium, copper, nickel, and zinc) in soil and plant samples an atomic spectrophotometric method was used. The samples were mineralized in aqua regia [10]. To analyze PAHs high-performance liquid chromatography with fluorometric detector was used. During the analysis the following equipment were used: a laboratory scale type XA 220 Radwag, an atomic absorption spectrophotometer Spectr AA10 Varian, mineralizer Vapodest Gerhard, and HPLC chromatograph Waters model Alliance 2695 with a fluorometric detector (HPLC-DAD).

2.5. PAHs analysis

The HPLC-DAD was used for PAHs qualification and quantification. Extraction of the samples was carried out in an ultrasonic bath with cyclohexane and dichloromethane mixtures as solvents. Prepared extracts were primarily concentrated under a nitrogen stream to a volume of 3 mL. Then those extracts were purified using SPE columns packed with silica gel in vacuum conditions. Subsequently extracts were concentrated again to a dry residue. Dry residue was then diluted in acetonitrile and used for chromatographic analysis. PAHs were qualified and quantified with a high-performance liquid chromatography method with a fluorometric detector. Identification of individual compounds was realized based on retention times of the compounds with retention times of standard solutions.

HPLC chromatograph Waters model Alliance 2695 with Supelcosil LC-PAH column (15 cm × 4.6 mm × 5 μm) was used. A fluorometric detector Waters 2475 and a photoindicator detector Waters 2,998 were used. The parameters of the instrumental method were as follows: time of analysis 40 min, time of stabilization 8 min. Flow velocity through the column was equal to 1.5 mL/min, temperature of column thermostating 25˚C. The fluorometric detector worked at wavelength of induction (extraction WL) equal to 275 nm and wavelength of emission (emission WL) equal to 350 nm.

To verify the method of samples' preparation for qualification and quantification of PAHs, some control samples with known concentration of PAH compounds were prepared. A standard mixture of PAHs (Accu Standard Inc. USA—PAH Mix) in benzene and dichloromethane (v/v 1:1) was spiked into soil amended with sewage sludge and into plant samples. The standard mixture was added to samples before adding the solvents and before they were extracted. Afterwards the samples were carefully shacked, extracted, and analyzed for PAHs according to the procedure described above. The recoveries of PAHs standard mixture for concentrations in samples varied from 77 to 103%. The average value was 85% which corresponds to the data found in the literature [6–9]. All analyses were done in triplicate. The following compounds were analyzed: acenaphtene, fluorene, phenantrene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(j)fluoranthene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene,

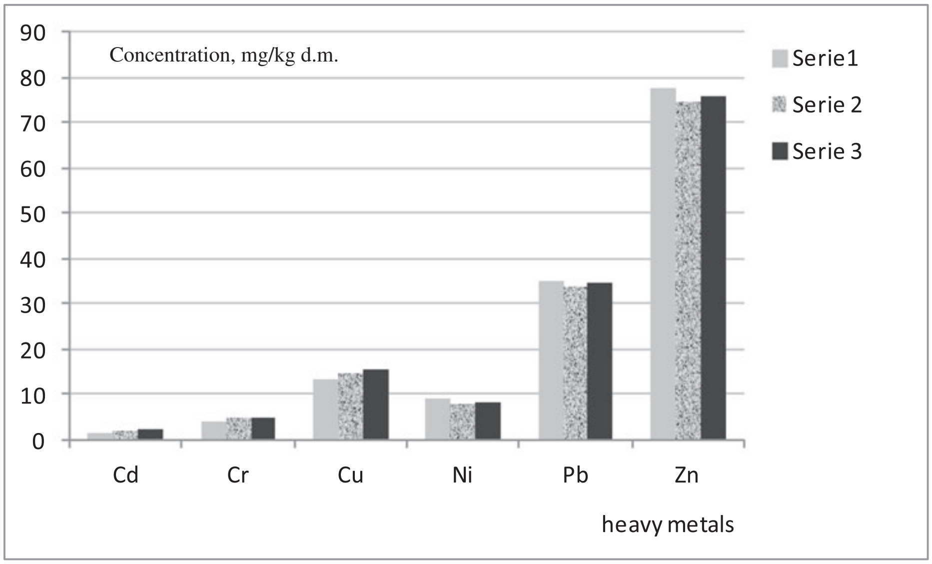

Fig. 5. Concentration of heavy metals in soil amended with sewage sludge.

dibenzo(ah)anthracene, benzo(ghi)perylene, and indeno(1,2,3, c,d)pyrene.

3. Results

3.1. Heavy metals in soil amended with sewage sludge

The concentrations of individual heavy metals in soil are presented in Fig. 5. Average concentration of individual heavy metals in soil was equal to: 1.81 mgCd/kg$_{d.m.}$, 14.46 mgCu/kg$_{d.m.}$, 8.29 mg Ni/kg$_{d.m.}$, 34.46 mgPb/kg$_{d.m.}$, and 76.10 mgZn/kg$_{d.m.}$. An increase of heavy metals' concentration in soil due to fertilization with sewage sludge was also stated by other authors [20,21]. An increase in individual heavy metals' concentration in soil is caused by amending the soil with sewage sludge as well as by the supply of metals with abscised leaves. Compared to the concentrations in soil collected before planting of the willows (Table 1) only the content of chromium decreased and was equal to 4.57 mg/kg$_{d.m.}$. A decrease in this metal concentration in soil after five years of plantation exploitation may be caused by its intensive accumulation in roots of the basket willow.

After five years of plantation exploitation the content of heavy metals still did not exceed permissible values set by the Regulation of the Minister of Environment of 1 August 2002 concerning municipal sewage sludge [10,19].

3.2. Heavy metals in plants

The content of heavy metals was analyzed in roots, stems, and leaves of *Salix viminalis* (Figs. 6–8). The results of other authors' investigations [2,3] confirm that there are significant differences in heavy metals' concentrations in particular parts of biomass. The highest average concentrations of selected heavy metals (cadmium, chromium, and nickel) were observed in roots: 0.90 mgCd/kg$_{d.m.}$, 10.94 mgCr/kg$_{d.m.}$, and 3.98 mgNi/kg$_{d.m.}$, respectively. The results concerning accumulation of cadmium and chromium in basket willow roots confirms the results obtained by other authors [22]. In the case of nickel, the results concerning its cumulation in roots of *S. viminalis* differ from the ones obtained in the present study. Some authors [2] indicate that nickel is mainly accumulated in stems of a basket willow planted on soil amended with sewage sludge.

The results obtained in our study indicate that stems of a basket willow do not accumulate high quantities of cadmium, chromium, copper, and lead. Concentrations of these elements were equal to 0.52, 8.01, 6.24, and 11.13 mg/kg$_{d.m.}$ for Cd, Cr, Cu, and Pb, respectively. During present investigations the presence of Ni in *S. viminalis* stems was observed.

Leaves of a basket willow contained the highest concentrations of copper (9.44 mgCh/kg$_{d.m.}$), lead (15.02 mgPb/kg$_{d.m.}$), and zinc (53.59 mgZn/kg$_{d.m.}$)—Fig. 8. Besides, the concentration of nickel in the leaves

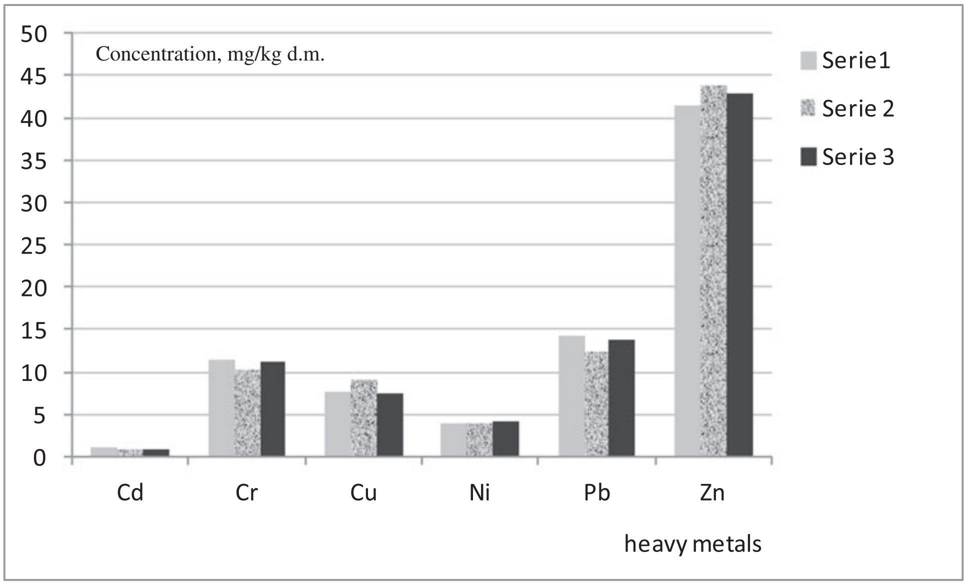

Fig. 6. Concentration of heavy metals in roots of *S. viminalis*.

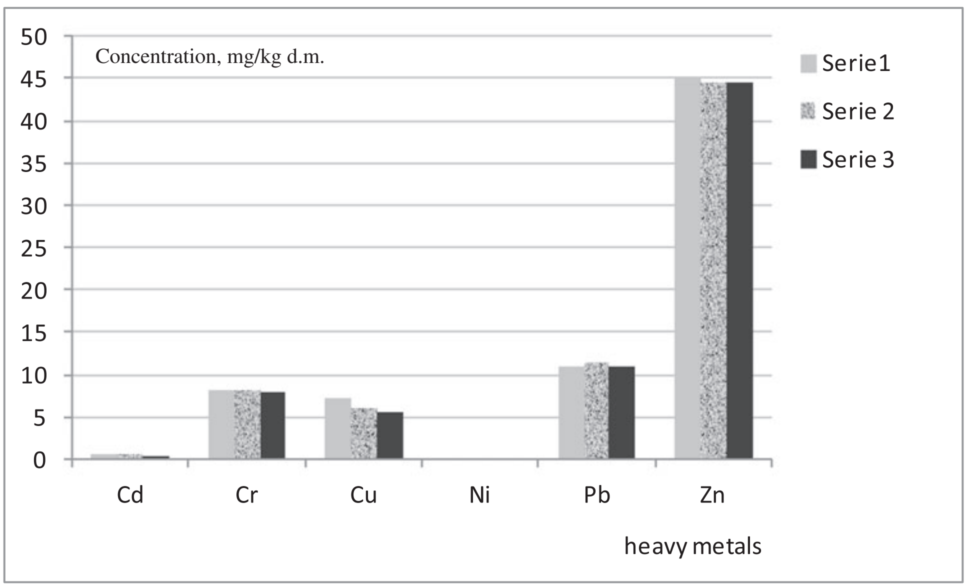

Fig. 7. Concentration of heavy metals in stems of *S. viminalis*.

was below detection level. Literature data [22] indicate that as lead concentration in soil increases the content of this element in plant does as well and the highest concentrations of Pb are present in roots. Copper behaves in the same way. The results of the present study indicated, however, that the highest concentration of these elements was observed in leaves.

3.3. PAHs in soil

In soil amended with sewage sludge only 15 of 16 PAHs analyzed were present. The total concentration of 15 PAHs varied between 631 and 686 $\mu g/kg_{d.m.}$. According to the classification of Institute of Soil Science and Plant Cultivation, the soils contaminated with PAHs at total concentration not higher

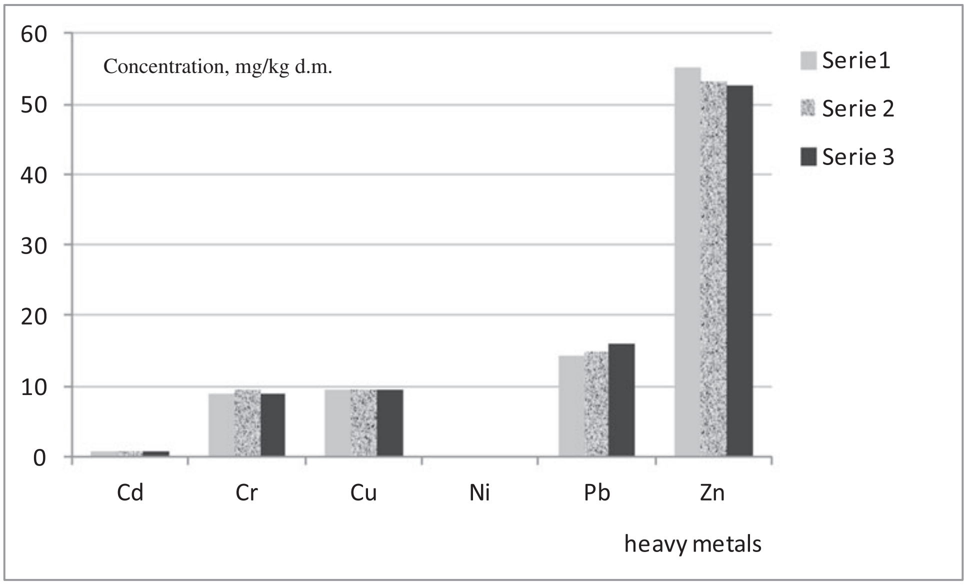

Fig. 8. Concentration of heavy metals in leaves of *S. viminalis*.

than 1,000 μg/kg$_{d.m.}$ can be recognized as not polluted [23]. Concentrations of individual PAHs in soil amended with sewage sludge are presented in Fig. 9.

It should be emphasized that permissible concentration of nine PAHs according to Polish standards concerning limit values of PAHs in soils from protected areas is also equal to 1,000 μg/kg$_{d.m.}$ However, other compounds were also taken into consideration during the investigation. They are (naphtalene, phenanthrene, anthracene, fluoranthene, chrysene, benzo(a) anthracene, benzo(a)fluoranthene, benzo(a)pyrene, and benzo(ghi)perylene) [24].

About 48% of total PAHs present in soil amended with sewage sludge were 4-ring compounds. PAHs classified as toxic constituted 54% of the total concentration of the hydrocarbons analyzes. The percentage share of the groups of hydrocarbons sorted according to the number of rings in their particles is presented in Table 3.

Concentration of bezno(a)pyrene varied between 46 and 49 μg/kg$_{d.m.}$ Fluoranthene was the compound which was observed in the highest concentration in the samples of soil amended with sewage sludge. This compound is not considered to be carcinogenic and it is usually present in soil at concentrations higher than other PAHs. Compared to Polish legislation standards it must be stated that the concentration of bezno(b)fluoranthne and fluoranthene in examined soil samples was above the permissible values for protected areas which are set at 20 μg/kg$_{d.m.}$ and 100 μg/kg$_{d.m}$, respectively. Moreover, the concentration of BaP exceeded the permissible value (30 μg/kg$_{d.m.}$) for arable and forest soils taken from the depth up to 0.3 m. In relation both to other depths and to industrial soils or soils situated in areas of influence of roads BaP concentration was 100–1,000 times lower [24].

When compared to the results obtained by other authors, the results obtained in the present study indicate that the concentration of PAHs was characteristic for the values from the areas not seriously polluted. The total PAHs concentrations in samples taken from the areas located close to routes of high traffic density, gas stations or air bases are significantly higher (even several hundred mg/kg$_{d.m.}$). In the case of arable soils, the total PAHs concentrations usually did not exceed 200 μg/kg$_{d.m.}$ Comparing PAHs concentrations analyzed in various studies is, however, difficult because PAHs are a very diversified group of compounds and various individual compounds are analyzed. Soils also had different properties, it was used in various ways and also the localization of sampling places in relation to pollution sources was diversified [12,25].

3.4. PAHs in plants

16 PAH compounds were present in roots, stems, and leaves of a basket willow. The highest concentration of PAHs total was obtained for leaves; it was on average equal to 116 μg/kg$_{d.m.}$. The total concentration of PAHs in stems was on average equal to 55 μg/kg$_{d.m.}$; in roots to 67 μg/kg$_{d.m.}$. Concentrations of individual

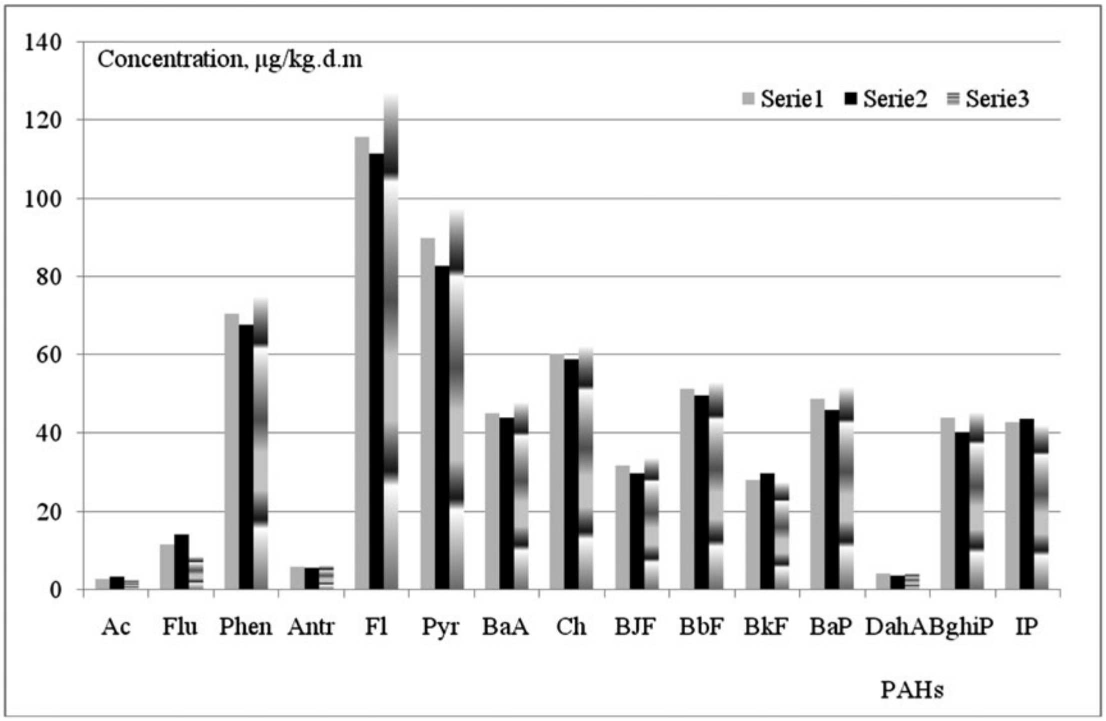

Fig. 9. Concentration of PAHs in soil amended with sewage sludge.

Table 3
Percentage share of the groups of hydrocarbons sorted according to the number of rings in their particles

PAHs	% Share in individual samples			
	Soil amended with sludge	Leaves	Stems	Roots
3-rings of PAHs	14	23	46	49
4-rings of PAHs	48	48	29	39
5-rings of PAHs	25	24	20	10
6-rings of PAHs	13	5	5	2
Carcinogenic PAHs	54	53	42	27

PAH compounds in leaves of *S. viminalis* are presented in Fig. 10. In leaves the dominant compound was fluoranthene. Carcinogenic compounds share reached 53% of PAHs total. The most abundant groups were 4-ring compounds with share of 48% of PAHs total. In Figs. 11 and 12, the concentrations of individual PAH compounds in stems and roots of *S. viminalis* are presented.

The dominant PAH compound in stems was fluoranthene. In roots the most abundant compound was phenantrene. The percentage share of the groups of hydrocarbons sorted according to the number of rings in their particles was different than in the case of soil and leaves (Table 3). The most abundant groups were 3-ring compounds (46–49% of PAHs total concentration). The share of carcinogenic compounds was lower than in soil and leaves and was equal to 42% (in the case of stems) and 27% for roots.

Literature data indicate a direct impact of soil and air pollution on PAHs content in plants. However, investigations are mainly focused on concentrations of these compounds in plants for consumption. It is especially important to evaluate PAHs levels in vegetables or fruits which are consumed without thermal processing, e.g. in lettuce, cabbage, tomatoes, cucumbers, potatoes, and berries. PAHs concentrations were also evaluated in grasses, crops, and legumes [12–15]. PAHs could be also synthesized by plants, however, compared to anthropogenic sources the quantities from natural ones are minute [26]. Migration of PAHs

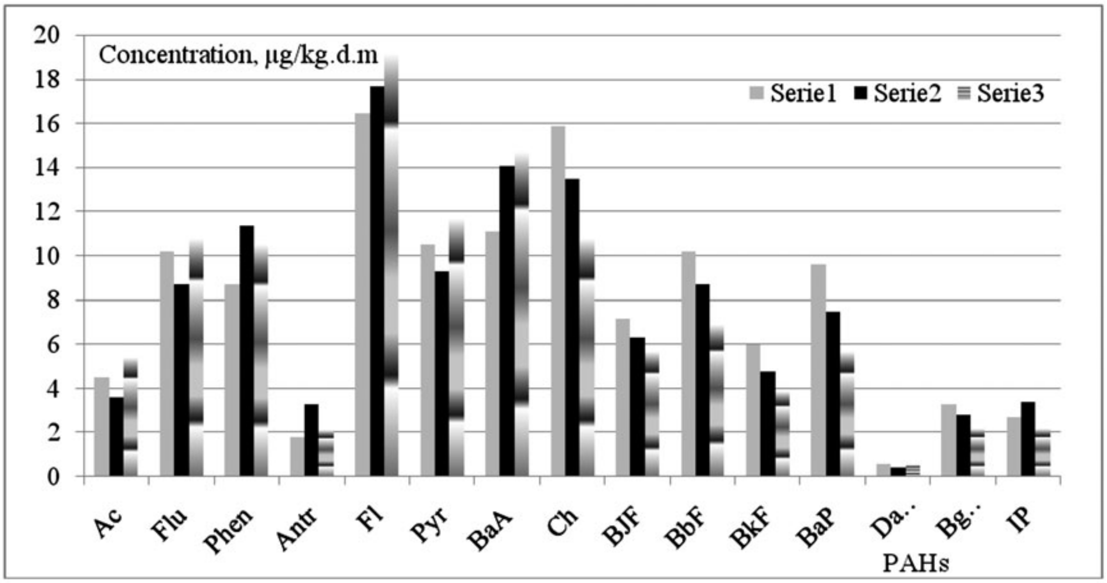

Fig. 10. Concentration of PAHs in leaves of *S. viminalis.*

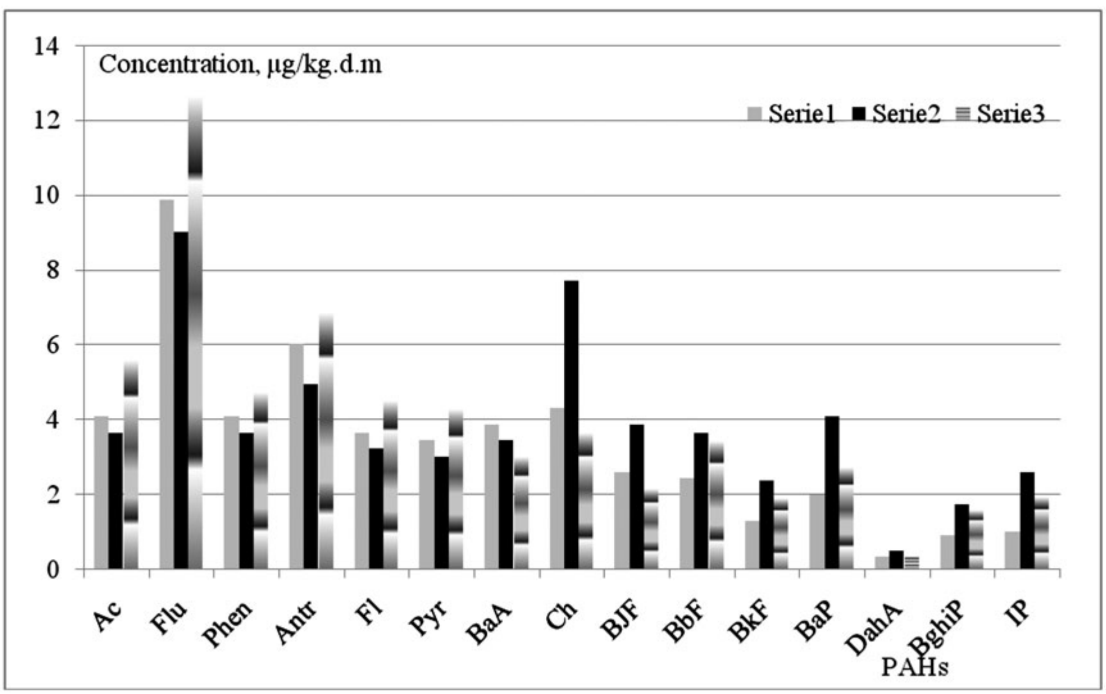

Fig. 11. Concentration of PAHs in stems of *S. viminalis.*

in plants' body was confirmed by several researchers. It was stated that hydrocarbons, which are compounds dissolve well in water, permeate into plant body and migrate within it more easily than non-soluble compounds. Compounds which are not well soluble in water are easier adsorbed on solid particles, accumulate on the surface of roots, and are not easy available for plants. Migration via roots into above surface parts of plants is possible mainly in the case of 2- and 3-ring PAHs. 4-, 5-, and 6-ring aromatic

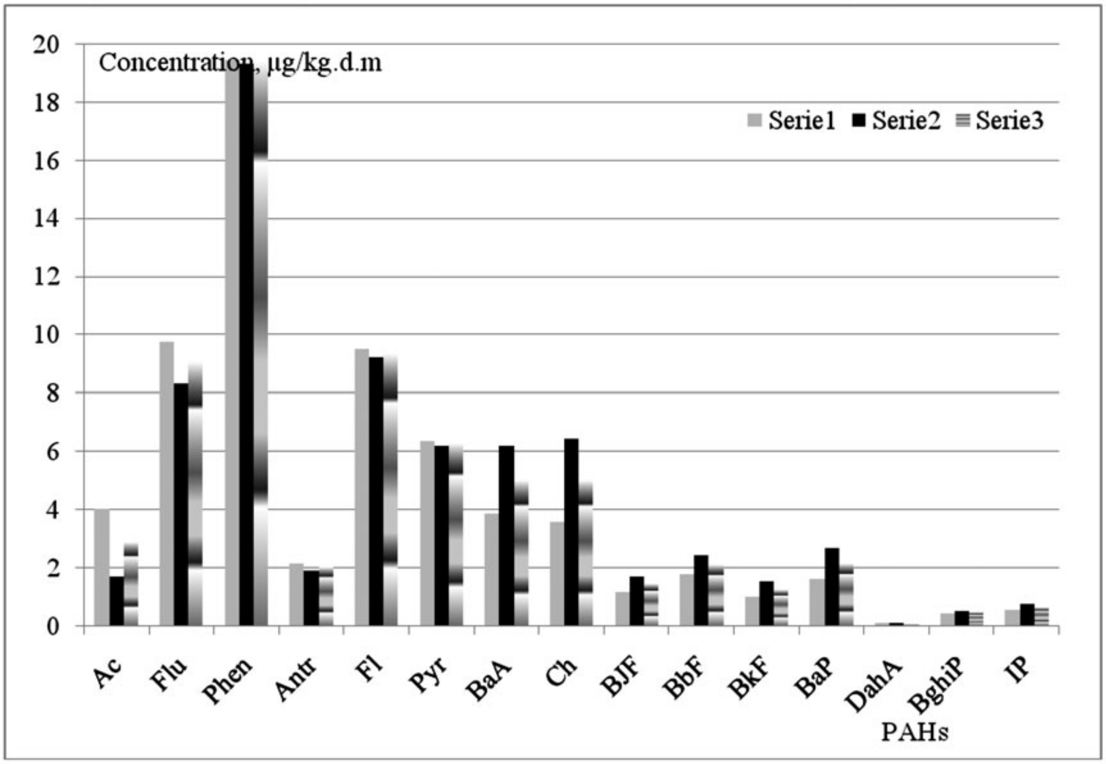

Fig. 12. Concentration of PAHs in roots of *S. viminalis.*

hydrocarbons are adsorbed on the surface of roots [27]. These facts were confirmed both by Tao et al. and by Klusek [13,28]. They determined the correlation between soil pollution with PAHs and concentration of these pollutants in vegetables. Investigations on phytoremediation indicated that plants are able to metabolize hydrocarbons via oxidation and in cometabolic processes. They can also accumulate by-products of hydrocarbons transformations. These transformations took place provided that PAHs are available for roots. Grasses, cereals, and legumes can significantly decrease PAHs concentration in polluted soils because roots of these plants stimulate the development of appropriate microflora by enzymes. As a result, some intensification of hydrocarbons' biodegradation occurs [17,29]. Also the results of investigations of Liste et al. confirm the correlation between effectiveness of PAHs biodegradation and presence of plants. In the work of Liste et al. oats, lupin, rape, dill, parsley, pepper, and pine were planted on soil contaminated with PAHs. Effectiveness of hydrocarbons removal was about twice higher in soil on which plants were planted. Investigations proved, moreover, that plants are able to accumulate hydrophobic compounds via transport from the roots system [14,15]. Maila et al. evaluated the relationship between germination of seeds and the level of soil pollution by PAHs. As PAHs concentration increased the germination rate of cress germination decreased [16].

4. Conclusions

During investigations on phytostabilization and phytoremediation of soils contaminated with heavy metals which concerns both immobilization of these compounds and their extraction, the following plants are usually used: white mustard (*Sinapis alba*), cabbage (*Brassica Juncea*), darnel ryegrass (*Lolium perenne*), fescue (*Festuca rubra*), tussock grass (*Poa pratnesis*), quinsland hemp (*Sida hermaphroodita*), miscanthus (*Spartina pectinata*) or basket willow (*S. viminalis*) [21,29]. Data concerning pollution of these plants with hydrocarbons on plantations of large area are missing. Some research work was undertaken to evaluate the effects of heavy metals on fates of PAHs in these plantations. Maliszewska-Kordybach et al. described the results of research work on effects of copper, zinc, lead, and cadmium salts on PAHs persistence in soil [12]. Lazzari et al. proved the relationship between PAHs and the presence of mercury, cadmium, lead, zinc, and copper in composted sewage sludge [9]. In both cases, it was stated that the presence of heavy metals inhibited PAHs degradation. The authors explained that the phenomenon is caused by a decrease in biological activity of the bacteria involved in PAHs degradation. Persistence of individual hydrocarbons was, however, diversified and the dynamics of their concentration changes during incubation was irregular [5,9,12].

Most research work is provided under laboratory conditions in the environment which is separated from any external environment. Soils are spiked with known quantities of PAHs and changes of their concentrations are monitored under set experimental conditions. Investigations in real environment are more difficult, and the clear-cut interpretation of the results is often impossible because of the variety of factors which have an impact on the changes in PAHs concentration.

During this experiment, the initial concentration of PAHs in substratum occurred due to the concentrations of these compounds both in soil and sewage sludge. Also air deposition played an important role in the initial concentration of PAHs. Both natural synthesis of these compounds and volatilization or leaching of PAHs into lower layers of soil could not be excluded. All these processes can cause a decrease in PAHs concentration in the surface layer of soil. In the air, PAHs are present mainly being adsorbed onto solid particles and as a result with air deposition (rain or dry deposition) PAHs concentration may increase also in leaves of plants. Although PAHs are ksenobiotics they undergo some transformations in various environmental conditions. These could be both biotic and abiotic transformations. Taking into consideration the presence of PAHs and heavy metals in substratum it can be stated that metals could inhibit the biodegradation of hydrocarbons.

At present, maximum values for PAHs in sewage sludge used in agriculture are not established. Only selected heavy metals' concentrations must be controlled in sewage sludge as well as the soil in the case of agricultural use of the sludge. However, the formulated proposals regarding some changes in EU Sludge Directive assume that also PAHs concentrations should be controlled in the sludge used in agriculture. Corrections in permissible concentrations of selected heavy metals (cadmium, chromium, copper, mercury, nickel, lead, and zinc) are also planned. The proposal assumes differentiation of heavy metals permissible concentrations in soil according to the pH value. The total permissible concentration of heavy metals in soil which will be amended with sewage sludge must be within 195.6 and 502.5 $mg/kg_{d.m.}$. According to this proposal, heavy metals mentioned above will also be analyzed in sewage sludge when it is used as a fertilizer. In this case, the maximum value of the total heavy metal's concentration should not exceed 5,570 mg/kgd.m. For PAHs the maximum concentration of the sum of acenaphtene, phenanthrene, fluorene, fluoranthene, pyrene, benzo(b + j + k)fluoranthene, benzo(a)pyrene, benzo(ghi)perylene, and indeno (1,2,3 c,d)pyrene is planned to be established at the value 6 $mg/kg_{d.m.}$ [30]. The maximum concentrations of PAHs are planned to be established only in the case of the agricultural use of sewage sludge. No maximum values are planned for planting plants which are not consumed.

Based on the results of the experiments it can be concluded that:

- after five years of *S. viminalis* planting in soil amended with sewage sludge an increase in most heavy metals' concentrations was stated. An increase by 19.27, 1.69, 9.1, 5.09, and 38.86 $mg/kg_{d.m.}$ was observed for Pb, Cd, Cu, Ni, and Zn, respectively,
- chromium concentration in soil amended with sewage sludge decreased (from 5.25 to 4.57 $mg/kg_{d.m.}$) after five years,
- compared to the concentration of individual heavy metals in soil amended with sewage sludge the content of these pollutants in *S. viminalis* biomass was lower. Average concentrations of cadmium, copper, nickel, lead, and zinc in some parts of a willow were equal to 0.71, 7.91, 1.33, 13.9, and 46.77 $mg/kg_{d.m.}$) respectively. Only chromium concentration (average 9.32 $mg/kg_{d.m.}$) in biomass was higher than in soil amended with sewage sludge,
- the total PAHs concentration in soil amended with sewage sludge was at the level of 657 $\mu g/kg_{d.m.}$; carcinogenic compounds shared 54% of the total concentration,
- the possibility of PAHs concentration both in above ground parts and roots of *S. viminalis* was confirmed,
- PAHs concentration in leaves (112–118 $\mu g/kg_{d.m.}$) was at average two times higher than in stems (49–59 $\mu g/kg_{d.m.}$) and roots (65–69 $\mu g/kg_{d.m.}$).

Supplementary information

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