Desalination and Water Treatment
www.deswater.com
doi: 10.1080/19443994.2014.883771

52 (2014) 3672–3679
May

Taylor & Francis
Taylor & Francis Group

Chromium as an inhibitor of PAHs degradation in deposed sewage sludge

Maria Włodarczyk-Makuła*

Department of Environmental Chemistry, Water and Wastewater Technology, Częstochowa University of Technology, 69 Dąbrowskiego Street, 42-200 Częstochowa, Poland
Tel. +48 34 32 50 919; Fax: +48 32 50 496; email: mwm@is.pcz.czest.pl

Received 20 December 2012; Accepted 4 July 2013

ABSTRACT

The aim of the investigation was to estimate the impact of the presence of chromium ions on decrease in PAHs concentration in sewage sludge stored under aerobic conditions. The studies were carried out using dewatered and biochemically stabilized sludges. The changes in the concentration of PAHs were followed in five series: in sludge samples taken after filter press (biotic samples—control samples), in sludge samples with added sodium azide (abiotic samples), in sludge with the addition of a standard PAH mixture, in sludge with added chromium(III) chloride, and in sludge with the addition of both the standard PAH mixture and Cr. The Cr was added into the sludges samples as a solution of chromium(III) chloride. The sludge samples were incubated for 12 weeks. Determination of PAHs in sludge samples was made at the beginning of the experiment (the initial concentration) and then six times over 2 weeks. The gas chromatography–mass spectrometry was used for qualification and quantification of PAHs. Six PAHs listed by EPA were identified: benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, dibenzo(a,h)anthracene, benzo(g,h,i)perylene, and indeno(1,2,3,c,d)pyrene. In sludges taken from municipal treatment plant, the average PAHs concentration was 289 μg/kg d.m. The inhibition of PAH degradation was found in sludges supplemented with chromium chloride (final average PAH concentration in modified sludges was four times higher than in the control sample).

Keywords: Sewage sludge; Chromium; BbF; BkF; BaP; DahA; BghiP; IP; Standard mixture of PAHs; Half-life; GC–MS

1. Introduction

In the literary sources there are many reports of PAHs content in sewage sludge. The presence of these compounds in sewage sludge is associated with the sorption on organic matter particles during wastewater treatment processes [1–3]. Although PAH in sewage sludge during digested processes is transformed, these compounds are also identified in high concentrations in digested sewage sludge (mg/kg d.m.). In the sewage sludge from large wastewater treatment plant (WTTP), micropollutants such as PAHs, polychlorbiphenyls (PCBs), heavy metals, and pathogenic organisms were identified

*Corresponding author.

Presented at the 11th Scientific Conference on Microcontaminants in Human Environment. 25–27 September 2013, Wisla, Poland
Organized by Department of Chemistry, Water and Wastewater Technology,
Faculty of Environmental Engineering and Biotechnology, Czestochowa University of Technology

1944-3994/1944-3986

[4–6]. This prevents the use of sludge in agriculture. In Polish legislation, the application of sewage sludge in agriculture is limited by permissible heavy metals (Zn, Pb, Cu, Cr, Hg, Ni, and Cd) concentrations (Table 1) and pathogens (*Salmonella*, *Ascaris* sp., *Trichuris* sp., *Toxocara* sp.) [7]. Proposed changes to EU Directive demand the control of toxic organic micropollutants in sewage sludge applied in agriculture including polycyclic aromatic hydrocarbons, PCBs, polychlorinated dibenzodioxins, polychlorinated dibenzofurans, di-(2-ethylexyl)phthalate, nonylphenols, adsorbable organic halogens, and linear alkylbenzene sulfonate [8]. Sewage sludge originating from municipal WTTPs is usually loaded with both heavy metals and PAHs. Therefore, it is important to investigate the behavior of hydrocarbons in the presence of metals when sewage sludge is stored.

PAHs are regarded as xenobiotics relatively resistant to the decomposition process that depends on both abiotic factors and the presence of micro-organisms [9–11]. The level of decomposition depends on physical–chemical hydrocarbon properties, the environment (water, soil, and air), and such environmental conditions as (humidity, temperature, light, and pH) [12,13]. There have only been a handful of investigations made concerning the impact of the occurrence or addition of some heavy metals on PAHs fates. Maliszewska-Kordybach et al. described the research into the effect of zinc, lead, and cadmium salts on PAHs persistence, but in relation to soil environment [14,15]. Lazzari et al. found a link between the presence of PAHs and mercury, cadmium, zinc, and copper in composted sewage sludge [16]. In both cases it turned out that the presence of metals inhibited the disappearance of PAHs′. This was due to the lower biological activity of bacteria responsible for the decomposition of these compounds. It was also found that individual hydrocarbons had varied sensitivity when metals were presented. The obtained results confirm the differential dependency between the concentration of individual hydrocarbons and the studied metals. A positive correlation among some metals (Cu, Cd, Zn, and Pb) and chrysene and benzo(k)fluoranthene (BkF) was found. Adsorption onto organic matter particles, biodegradation and, at a lower level, volatilization are regarded as the processes responsible for changes in PAHs concentration during composting. It was found that the intensity of the above mentioned processes depends on the number of rings in the molecule [14–18]. Stability of PAHs is defined as half-life of their decomposition. The available investigations take into account mainly soils or the mixture of soil and sewage sludge. It was found that half-lives of PAHs were in the range of 3–3,111 d and of 15–408 d in mixture of soil with sewage sludge and in soil, respectively [14,15]. In the earlier investigation, in biotic samples the half-time of carcinogenic hydrocarbons was in the range of 17–126 d. Half-life of these compounds in abiotic sewage sludges was in the range of 32–2,048 d [19]. The objective of this work was to find out the impact of the addition of chromium chloride (in concentrations exceeding permissible levels) on PAHs depletion in sewage sludge stored under aerobic conditions (with standard mixture of PAHs and without standard mixture of PAHs). Under experimental conditions the half-lives of individual compounds were diverse.

2. Materials and methods

2.1. Materials

The investigations were carried out under laboratory conditions using dewatered sewage sludge formerly stabilized in a aerobic digestion process.

Table 1
Concentration of PAHs in sewage sludge and limits of metals concentration used in agriculture in Polish and EU legislations, mg/kg d.m.

Metals	Sewage sludge taken from WWTP	Use of sewage sludge Polish legislation [7]			EU Directive 86/278/EWG [20]	Proposal of changes of EU Directive [8]
		In agriculture	Recultivation	Other		
Chromium	122.0	500	1,000	2,500	–	1,000
Zinc	1422.0	2,500	3,500	5,000	250–4,000	2,500
Cadmium	1.0	20	25	50	20–40	10
Copper	149.0	1,000	1,200	2,000	1,000–1,750	1,000
Lead	15.6	750	1,000	1,500	750–1,200	750
Mercury	0.3	16	20	25	16–25	10
Nickel	38.3	300	400	500	300–400	300

Sludge samples were a one-off batch taken from small municipal WTTP. The sludge was primary analyzed for: hydratation, pH, alkalinity, acidity, and contents of organic compounds. The contents of total selected heavy metals were also determined. The sludge originating from WWTP had a low water content (83%). Sewage sludge were dewatered sludge after prior biochemical stabilization. The same was found for alkanity (55 mval/L) and pH = 8.4. Organic matter content of 52% proved that the sludge was well digested. The comparison of the concentration of selected metals in sludge and the legislation (Polish and EU Directive) limits for municipal sludge in agriculture is presented in Table 1. The sludge had a low chromium concentration (122 mg/kg d.m.) and other metals concentration was also below permissible levels for sludge applied in agriculture and recultivation areas assigned for agricultural purposes [7,8].

2.2. Experimental procedure

Sludge samples were homogenized and representative samples were selected. Afterwards, 70 samples of 10 g each were prepared, and put into 200 mL glass flasks in order to be protected from photodegradation and volatilization. A chromium(III) chloride solution equal to 500 mg of Cr/kg of dry matter (d.m.) (including original Cr concentration) was added to 28 sludge samples. A standard mixture of 16 PAH compounds in benzene and dichloromethane in the concentration of 2,000 μg/mL each was added to 14 samples. The standard mixture dose was 10,000 μg/kg d.m. The same dose of the standard mixture was also added to the 14 remaining sludge samples.

The sodium azide was added to 14 samples to inhibit microbial activity (abiotic samples). The samples not amended with chromium salt nor supplemented with standard mixture were treated as control samples. All the samples were incubated for 90 d at 20˚C in the dark in order to limit photovolatilization. Hydratation was kept constant at this time. The whole volume of each sludge sample was used to determine PAHs. PAH samples were taken at the beginning of the experiment (the initial concentration) and six times at two weeks intervals (after 2, 4, 6, 8, 10, and 12 weeks). The following investigations were made:

- determination of changes in PAH concentrations in sewage sludge samples taken from WWTP (biotic—control samples),
- determination of changes in PAH concentrations in sewage sludge samples taken from WWTP with added sodium azide (abiotic samples),
- determination of changes in PAH concentrations in sewage sludge samples with added chromium,
- determination of changes in PAH concentrations in sewage sludge samples taken from WWTP and supplemented with a standard mixture of these compounds, and
- determination of changes in PAH concentrations in sewage sludge samples taken from WWTP and supported the standard mixture of these compounds as well as chromium.

2.3. Calculation of PAHs half-life

Assuming that the decomposition speed of substrate (PAHs) takes place according to the first-order reaction. Half-life $T_{1/2}$ of hydrocarbons was calculated according to the following equations [14]:

$$T_{1/2} = \ln\frac{2}{k} \text{ and } \ln\frac{C_0}{C_t} = k \cdot t$$

where C_0—initial concentration of PAHs [μg/kg dm]; C_t—PAHs concentration in sewage sludge after t days of sewage sludge incubation [μg/kg d.m.]; t—time of incubation of sewage sludge [d]; and k—the reaction rate constant [d^{-1}].

2.4. Statistical methods

A *student t-test* was used in order to assess the statistical significance of the results. The comparison of affectivities of PAHs degradation in the presence of chromium chloride and micro-organisms and with standard mixture was calculated according to *t-test*. The critical value was read from tables for specified degree of freedom ($n-2$) and at a confidence level of 95%. Theoretical value of decomposition t_d ranged 4,303 [21].

2.5. PAHs analysis

The gas chromatography–mass spectrometry was used for qualification and quantification of PAHs. The extraction process for samples was carried out in ultrasonic bath with cyclohexane and dichloromethane mixture as solvents. Prepared extracts were primarily concentrated under nitrogen stream to a volume of 3 mL. The extracts were then purified by using SPE columns packed with silica gel in vacuum conditions. Subsequently those extracts were concentrated again to a volume 1 mL. For chromatographic determination of individual PAHs GC 8000 gas chromatograph

Fisons equipped with a mass spectrometric detector MD 800 was used. The parameters of chromatographic analysis were as follows: carrier gas—helium 70 kPa, temperature program 40–120˚C (40˚C/min) to 280˚C (5˚C/min), and 280˚C for 20 min, volume injection—1 µL, injection system—on column injector, interface temperature—280˚C, column—DB-5 (30 m; 0.25 mm; 0.25 µm), integration system—MassLab. The following PAHs according to US EPA list were analyzed [22]:

- 5-ring hydrocarbons: benzo(b)fluoranthene (BbF), BkF, benzo(a)pyrene (BaP), dibenzo(a,h)anthracene (DahA).
- 6-ring hydrocarbons: indeno(1,2,3,c,d)pyrene (IP), benzo(g,h,i)perylene (Bper).

To verify the method of preparation of samples for qualification and quantification of PAHs control, the samples with determined concentration of PAH compounds were prepared. Standard mixture of PAHs (Accu Standard Inc. USA—PAH Mix) in benzene and dichloromethane (v/v 1:1) was spiked into sewage sludge samples. Standard mixture concentration spiked into the sewage sludge samples was equal to 10 mg/kg d.m. The standard mixture was added to samples before adding the solvents and extraction process. Then, 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 sludges taken from WWTP varied from 75 to 104%. The average value was 85% which corresponds and confirms the previously obtained data found in literary sources [5,14].

3. Results

The average total concentration of 16 PAHs in sludges taken from WWTP does not exceed 1,000 µg/kg d.m. which corresponds with the results of other authors as well as our own experiments [4,5,19]. The concentration of 5-rings and 6-rings of hydrocarbons were in the range 112–180 and 86–90 µg/kg d.m., respectively. The dynamic of concentration changes of individual hydrocarbon in the control samples as well as those with added chromium are given in Figs. 1 and 2. Gradually, lower concentration of the six-studied PAHs was determined during incubation of the samples under oxygen conditions. In the initial step of the investigation (after 2 weeks), the total PAHs concentration in the control sludges was lower than the initial ones of 27%. After 15 d incubation of samples in controlled sludge samples, the average concentration of PAHs was 289 µg/kg d.m. At the same time, the

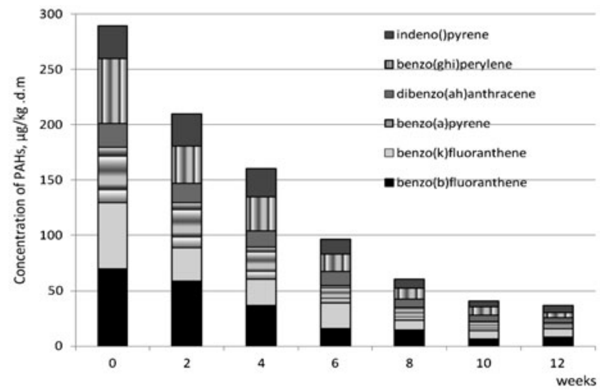

Fig. 1. Changes in concentration of 5- and 6-rings of PAHs in sewage sludge—control samples.

average PAHs concentration in sludges supported with Cr, was 366 µg/kg d.m. Some fluctuations in hydrocarbons concentrations may occur due to its periodic formation of by-products of the decomposition of other complex PAHs and/or destruction of micro-organism in the presence of chromium as well as the release of this compound from the cells [23]. Significantly lower PAH concentrations were found after further incubation time, mainly in control sludges. At the end of sewage sludge incubation, the total concentrations of 5-ring hydrocarbons were 87 and 47% lower than the initial one in control samples and in samples with added chromium chloride, respectively. The percentage decrease in concentration of 6-rings hydrocarbons were from two times up to three times lower in the sludge samples with added chromium than in the control samples.

A student *t*-test was used in order to assess the statistically significant differences between the initial and final PAH concentrations as well as in order to estimate the statistically significant presence of chromium chloride in sludges after 90 d of incubation.

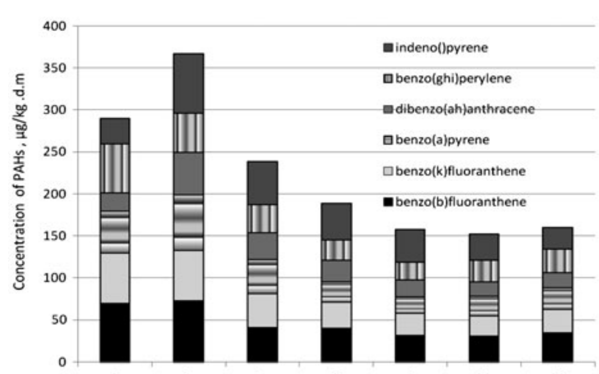

Fig. 2. Changes in concentration of 5- and 6-rings of PAHs in sewage sludge with chromium.

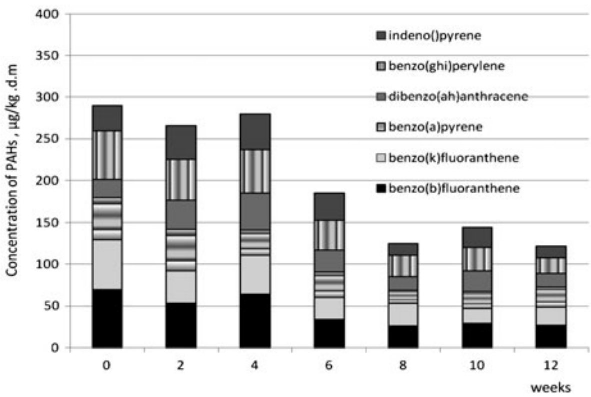

Fig. 3. Changes in concentration of 5- and 6-ring of PAHs in abiotic sewage sludge.

It was estimated that changes in 5- and 6-ring hydrocarbons concentrations between the initial and final concentration differed significantly in the control sludges and in sludges with added chromium chloride.

In Fig. 3, the changes of PAHs concentration during incubation of abiotic sewage sludge (with sodium azide) are presented. In the abiotic sludge samples with sodium azide after 2 and after 4 weeks, the total PAH concentrations were at the same level as initial content. At this time the sum of concentration of 5-ring and 6-ring of hydrocarbons were in the range from 266 to 289 μg/kg d.m.

At the end of experiment, the concentration of 5-ring and 6-rings of PAHs were 72 and 78% lower than initial ones, respectively. Comparing the loss of individual PAHs in sewage sludge under biotic and abiotic conditions it can be concluded that during the incubation which was recorded by analyzing the concentrations at fixed intervals, significant losses of these compounds were associated with physical and chemical transformations (Figs. 1 and 3). Among the physicochemical processes, the most significant are chemical reaction of hydrocarbons with other compounds of sewage sludges, volatilization of hydrocarbons, and sorption on solid particles. Sorption of PAHs on the particles is so strong that it hinders the extraction of these compounds to organic solvents during reparation of samples. 5- and 6-ring of hydrocarbons characterized by high values of the coefficient of octanol/water (6.04–7.66) shows some affinity for the solid particles. The chemical reactions of PAHs with other components of sewage sludge are the following: oxidation, connecting, substitution (chlorination, nitration, sulphonation, alkylation) [24]. The biodegradability of these compounds is also possible but the efficiency of this process is lower. There could be two-way biological changes: on one hand, there may be the release of PAHs from microbial cells after their breakup or—enzymatic degradation of hydrocarbons in liquid phase during incubation [11,22].

A student *t*-test was used in order to assess the statistically significant differences between the initial and final PAH concentrations as well as in order to estimate the statistically significant presence of micro-organisms in sludges. It was estimated that changes in 5- and 6-ring hydrocarbons between the initial and final concentration differed significantly in the abiotic sewage sludges. The addition of sodium azide had significant impact on changes in 5- and 6-rings of PAHs concentrations. Therefore, statistical analysis shows the importance of abiotic processes in the losses of PAHs. The differences between the concentrations of PAHs in biotic and abiotic sewage sludges were not significant. This indicates the

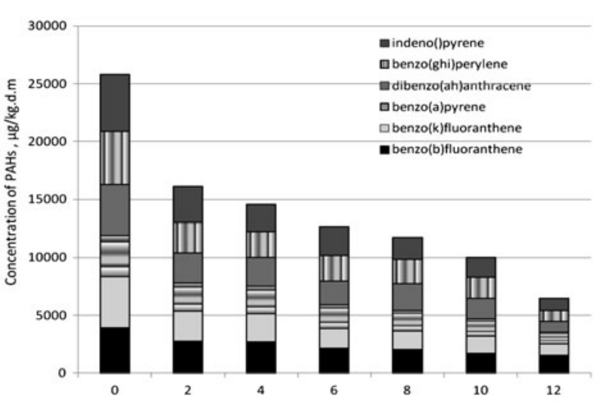

Fig. 4. Changes in concentration of 5- and 6-rings of PAHs in sewage sludge amended with standard mixture.

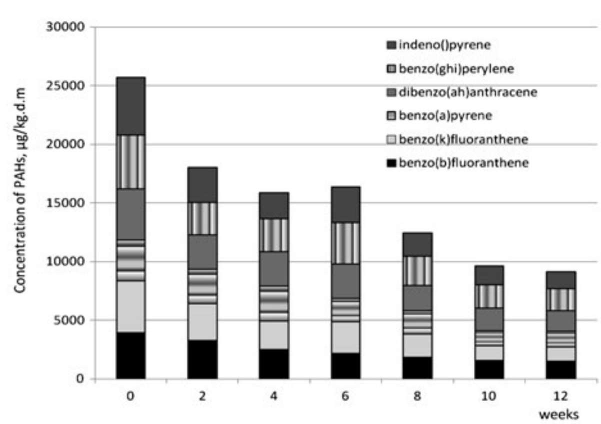

Fig. 5. Changes in concentration of 5- and 6-rings of PAHs in sewage sludge both amended with standard mixture of PAHs and chromium.

relatively low importance of biological effects in the removal of hydrocarbons.

The dynamics of hydrocarbon changes in sludges supplemented with the standard mixture with and without chromium chloride addition are given in Figs. 4 and 5.

The initial PAHs concentration in sludges supported with the standard mixture was 25,789 μg/kg d.m. The gradually lower concentration of PAHs was determined during the incubation of the samples irrespective of the occurrence of chromium. The differences in results between the total hydrocarbons determination in sludges with and without added chromium did not exceed 12%. After 90 d of incubation of hydrocarbons, concentration in sludges with added chromium and the standard mixture was 1.5 times higher than in samples sludges without chromium. The final 6-rings PAHs concentration in sewage sludge with standard mixture and in sewage sludge amended both with standard mixture and chromium chloride were 5,747 and 9,174 μg/kg d.m., respectively. In sewage sludge amended with standard mixture of PAHs, the decrease of 5-ring and 6-rings of hydrocarbons were 77 and 79% respectively, whereas the loses of hydrocarbons in sewage sludge with chromium were 64 and 65%, respectively.

The statistical analysis shows that there are no significant differences in sludges augmented with the standard mixture among the concentration of hydrocarbons in the both sludges (without and with added Cr) during deposed of sewage sludges. There is a significant difference between the total contents of six hydrocarbons before and after incubation. In Table 2, percentages of removal of hydrocarbons changes are grouped according to ring numbers are presented.

The percentage decrease in hydrocarbons was twice lower in the sludge samples with added chromium than in the control samples. In samples amended with standard mixture, the percentage decrease in total of 5- and 6-ring hydrocarbons concentration was 1.2 times higher than in the presence of Cr. In Table 3, the half-life in biotic sewage sludge and sewage sludge with chromium chloride of investigated hydrocarbons are presented.

Ranges of value of time decomposition were determined for various time intervals of sewage sludges storage (6 intervals). The half-life of hydrocarbons was the lowest in control samples. For example, the half-time of BbF corresponded to 49 d in biologically active sewage sludge samples, whereas in sewage sludge amended with chromium chloride $T_{1/2}$ reached 76 d. In abiotic sewage sludge, half-life was 75 d. Half-time of BkF reached 5,000 d in sewage sludge with chromium chloride. During the deposition of sewage sludge containing chromium concentration of indeno (123cd)pyrene were higher than the initial content therefore not calculated half-life time of this hydrocarbon. IP and BkF were the most persistent hydrocarbons. In Table 3, t_d values calculated for PAHs concentration in sewage sludges amended with standard mixture of PAHs and in sewage sludge amended both standard mixture of PAHs and chromium chloride in set time intervals are presented. The half-time of hydrocarbons was in the range of 18–83 d in sewage sludge amended with standard mixture. In sewage sludge with standard mixture and chromium chloride, the half-time was in the range of 20–215 d. BaP was the most persistent hydrocarbon, the half-time was the highest. Among investigated hydrocarbons, the highest life-time equal to 5,001 d was determined for BbF in biotic sewage sludge samples with chromium. The results correspond with earlier investigation, the most persistent were BaP and BbF [19].

In sludges without the standard mixture, the presence of Cr had a significant impact on the studied hydrocarbons and on the changes in the total PAHs contents after 90 d of incubation. This might have been due to the selective limitation of micro-organisms activity that causes decomposition of individual groups of these compounds. Moreover, the following

Table 2
Removal of PAHs in sewage sludge (%)

Samples	PAHs: 5-ring of PAHs: B(b)F, B(k)F, B(a)P, D(a,h)A	6-ring of PAHs: B(g,h,i)P, IP	Total of 6 PAHs
Sewage sludge—control (biotic) samples	87 (88, 87, 90, 79)	88 (79, 92)	87
Sewage sludge—biotic samples with $CrCl_3$	47 (44, 53, 41, 9)	39 (42, 14)	44
Abiotic samples	72 (73, 74, 67, 73)	78 (74, 81)	74
Sludge with standard mixture	77 (79, 77, 68, 80)	79 (78, 80)	77
Sludge with both standard mixture of PAHs and $CrCl_3$	64 (65, 75, 68, 66)	65 (71, 74)	64

Table 3
Half-life of hydrocarbons in sewage sludge

Sewage sludge	Weeks of incubation	Half-life of hydrocarbons, day					
		BbF	BkF	BaP	DahA	BghiP	IP
Control (biotic) samples	2	43	15	55	45	19	407
	4	37	29	110	91	37	844
	6	49	34	56	81	48	202
	8	28	43	36	74	32	53
	10	33	27	36	51	29	42
	12	27	29	35	48	30	37
Biotic samples with $CrCl_3$	2	–	2,500	–	–	48	–
	4	–	5,001	–	–	95	–
	6	58	81	146	-	54	–
	8	75	63	59	-	47	–
	10	66	63	56	545	52	–
	12	76	68	86	216	77	–
Abiotic samples	2	17	13	26	18	27	18
	4	34	26	52	35	54	36
	6	75	53	34	98	99	62
	8	39	35	47	49	60	50
	10	39	46	34	38	50	32
	12	52	45	49	72	67	57
Sludge with standard mixture	2	30	20	27	20	19	23
	4	59	39	55	40	37	45
	6	83	53	77	56	42	41
	8	70	44	77	54	58	61
	10	79	51	77	80	68	53
	12	75	57	72	69	67	60
Sludge with both standard mixture of PAH and $CrCl_3$	2	59	30	66	26	20	21
	4	118	59	131	52	40	42
	6	70	52	215	78	62	40
	8	69	87	72	104	161	85
	10	68	66	93	74	82	58
	12	67	50	64	74	76	56

phenomenon: sorption onto particles, volatilization, and the possibility of binding with chlorine and formation of PAHs-related compounds which were not analyzed, cannot be excluded. In sludges supplemented with the standard mixture, no significant differences were found between the total PAH contents in the sludges samples and in the samples with added Cr. Thus, it is suggested that investigations into the dynamics of changes of PAH concentration in sludges should be carried out without an additional amount of hydrocarbons. The results are similar to the literary sources [14–18] concerning the behavior of PAHs' in soil contaminated with heavy metals as well as in the sewage sludge composting process. It is stated that the stability of individual hydrocarbons could vary and the dynamic of changes of concentrations during incubation of studied materials could be irregular [25,26].

4. Conclusions

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

(1) Significant differences between initial concentrations and final concentrations for 5- and 6-ring PAHs in control samples and in samples with added chromium were observed.
(2) The inhibition of PAH degradation was found in sludges supplemented with chromium chloride (final average PAH concentration in modified sludges was twice higher than in the control sample).
(3) The dynamic of hydrocarbon changes in sewage sludges supplemented with the standard mixture was similar to those observed in the sludges both with and without chromium addition.

(4) The presence of chromium has a statistically significant impact on the total 5- and 6-rings of hydrocarbons in sludges supplemented with the standard mixture (final average PAH concentration in modified sludges was 1.2 times higher than in the sewage sludge without chromium).

Acknowledgement

This research was supported by the Committee of Scientific Research grant 4 TO9D-040-24 and BS-PB-402-301/11.

References

[1] B.V. Chang, S.W. Chang, S.Y. Yuan, Anaerobic biodegradation of polycyclic aromatic hydrocarbons in sludge, Adv. Environ. Res. 7 (2003) 623–628.

[2] E. Trably, D. Patureau, Successful treatment of low PAH-contaminated sewage sludge in aerobic bioreactors, Environ. Sci. Pollut. Res. Int. 3 (2006) 170–176.

[3] P. Conte, A. Zena, G. Pilidis, A. Piccolo, Increased retention of polycyclic aromatic hydrocarbons in soils induced by soil treatment with humic substances, Environ. Pollut. 112 (2001) 27–31.

[4] S. Pérez, M. Guillamón, D. Barceló, Quantitative analysis of polycyclic aromatic hydrocarbons in sewage sludge from wastewater treatment plants, J. Chromatogr. A 938 (2001) 57–65.

[5] M. Włodarczyk-Makuła, M. Janosz-Rajczyk, The impact of sludges added to the soil on the changes of selected organic pollutants, Pol. J. Environ. Stud. 2A (2007) 682–685.

[6] L. Hua, W.X. Wu, X.Y. Liu, C.M. Tientchen, Y.X. Chen, Heavy metals and PAHs in sewage sludge from twelve wastewater treatment plants in Zhejiang Province, Biomed. Environ. Sci. 21 (2008) 345–352.

[7] Dz. U Nr 137 poz. 924, Regulation of the Minister of Environment on Municipal Sewage Sludge, 2010 (in Polish).

[8] A. Bernal-Martinez, D. Patureau, J.P. Delgenès, H. Carrère, Removal of polycyclic aromatic hydrocarbons (PAH) during anaerobic digestion with recirculation of ozonated sewage sludge, J. Hazard. Mater. 162 (2009) 1145–1150.

[9] E.H. Lee, J. Kim, K.S. Cho, Y.G. Ahn, G.S. Hwang, Degradation of hexane and other recalcitrant hydrocarbons by a novel isolate, *Rhodococcus* sp. EH831, Environ. Sci. Pollut. Res. 17 (2010) 64–77.

[10] A. Feilberg, T. Nielsen, Photodegradation of nitro-PAHs in viscous organic media used as models of organic aerosols, Environ. Sci. Technol. 35 (2001) 108–113.

[11] A. Kornmüller, U. Wiesmann, Continuous ozonation of polycyclic aromatic hydrocarbons in oil/water-emulsions and biodegradation of oxidation products, Water Sci. Technol. 40 (1999) 107–114.

[12] A. Bernal-Martinez, H. Carrère, D. Patureau, J.P. Delgenès, Combining anaerobic digestion and ozonation to remove PAH from urban sludge, Process Biochem. 40 (2005) 3244–3250.

[13] J.J.H. Haftka, H.A.J. Govers, J.R. Parsons, Influence of temperature and origin of dissolved organic matter on the partitioning behavior of polycyclic aromatic hydrocarbons, Environ. Sci. Pollut. Res. 17 (2010) 1070–1079.

[14] B. Maliszewska-Kordybach, The effect of temperature on the rate of disappearance of polycyclic aromatic hydrocarbons from soils, Environ. Pollut. 79 (1993) 15–20.

[15] L. Lazzari, L. Sperni, P. Bertin, B. Pavoni, Correlation between inorganic (heavy metals) and organic (PCBs and PAHs) micropollutant concentrations during sewage sludge composting processes, Chemosphere 41 (2000) 427–435.

[16] B.V. Chang, S.W. Chang, S.Y. Yuan, Anaerobic degradation of polycyclic aromatic hydrocarbons in sludge, Adv. Environ. Res. 7 (2003) 623–628.

[17] K.B. Chipasa, Accumulation and fate of selected heavy metals in a biological wastewater treatment system, Waste Manage. 23(2) (2003) 135–143.

[18] J.-Y. Wang, D.-S. Zhang, O. Stabnikova, J.-H. Tay, Evaluation of electrokinetic removal of heavy metals from sewage sludge, J. Hazard. Mater. 124(1–3) (2005) 139–146.

[19] M. Włodarczyk-Makuła, Half-time of carcinogenic PAHs in stored sewage sludge, Arch. Environ. Prot. 38(2) (2012) 33–44.

[20] Regulation (EC) No. 850/2004 of the European Parliament and of the Council of 29 April 2004 on Persistent Organic Pollutants and Amending Directive 79/117/EEC.

[21] D. Bochenek, M. Falandysz, A. Górska, G. Jabłonowski, M. Jasiński, K. Karczewska, A. Kiełczykowska, D. Kotlewski, M. Lizuraj, T. Pac, T. Pawłowska, T. Skwarka, J. Sulik, M. Wojciechowska, P. Wrzosek, Statistical Information and Elaborations Environment, Central Statistical Office, Warsaw, 2010.

[22] M.T. Pena, M.C. Casais, M.C. Mejuto, R. Cela, Development of a matrix solid-phase dispersion method for the determination of polycyclic aromatic hydrocarbons in sewage sludge samples, Anal. Chim. Acta 626 (2008) 155–165.

[23] T.M. Traczewska, Biotoxicity of products of transformation of anthracene and phenanthrene in water as well as their possible removal, Technical University of Wroclaw, Monographs, 2003.

[24] S. Baran, J.E. Bielińska, P. Oleszczuk, Enzymatic activity in an airfield soil polluted with polycyclic aromatic hydrocarbons, Geoderma 118 (2004) 221–232.

[25] P. Oleszczuk, Application of three methods used for the evaluation of polycyclic aromatic hydrocarbons (PAHs) bioaccessibility for sewage sludge composting, Bioresour. Technol. 100 (2009) 413–420.

[26] J.M. Park, S.B. Lee, J.P. Kim, M.J. Kim, O.S. Kwon, D.I. Jung, Behaviour of PAHs from sewage sludge incinerators in Korea, Waste Manage. 29 (2009) 690–695.