



Sorption of phenanthrene by sewage sludge during composting in relation to potentially bioavailable contaminant content

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ABSTRACT

The aim of the present study was to determine to what degree the sewage sludge sorption capacity to phenanthrene influences on bioavailability of this compound during composting. Sewage sludges were composted for 76 days. The content of the potentially bioavailable phenanthrene fraction was determined by: mild-solvent extraction with *n*-butanol (BTL) and non-exhaustive extraction technique with hydroxypropyl[β] cyclodextrin (HPCD). Batch experiments were used to construct phenanthrene sorption isotherms. The contribution of the potentially bioavailable phenanthrene fraction in individual sewage sludges ranged from 32 to 48% (BTL) and from 5.1 to 80.3% (HPCD). The direction of changes in the potentially bioavailable fraction resulting from composting also depended on the sewage sludge and the extraction method applied. Isotherms demonstrated a good fit to the Freundlich isotherm model. Sorption coefficients ($\log K_F$) and organic carbon-normalized distribution coefficients ($\log K_{oc}$) of phenanthrene by sewage sludges ranged from 3.42 to 3.98 and from 4.14 to 4.70, respectively. Sewage sludges exhibited relatively strong affinity for sorption large amounts of phenanthrene. In the case of two sludges, a strong relationship between phenanthrene sorption capacity ($\log K_F$ and $\log K_{oc}$) and the content of the bioavailable fraction of this compound was observed.

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1. Introduction

Sewage sludge is the byproduct of the process of wastewater treatment. The increased rate of sewage sludges production is a matter of great concern whenever the aspect of final disposal is considered. Due to the presence of pollutants, sewage sludge land application may be forbidden. For this reason it is necessary to look for a solution which can optimize sludge properties in this respect. The method of sewage sludges composting is a cheap and simple method of such optimization of sludge properties, as well as of sludge decontamination. In numerous studies it has been shown that composting is an efficient method of reducing the presence of such compounds as polycyclic aromatic hydrocarbons, 4-nonylphenols, phthalic acid esters and polychlorinated biphenyls [1–6]. Polycyclic aromatic hydrocarbons (PAH) are common contaminants in sewage sludges. They get into sludges from domestic wastewater and trade effluent, through deposition and run-off into storm drains and from formation of precursors in wastewater. In the literature, it has been shown that PAH levels in sewage sludges are high enough to limit their utilization in

the natural environment [7,8]. Application of sewage sludges as fertilizers can lead to PAHs accumulation in the soils [9–11], as well as their migration to the food chain [12,13]. Composting has been proved to degrade PAHs at a rate from several to over 90% [4,5,14], lowering the content to a level accepted by the EU draft [15].

PAHs removals observed during composting may be the result of biodegradation of contaminants, but also similarly as in the soils, pollutants may have been converted into bound residues or a part of them may have been sequestered [6,14]. Contaminant sorption/desorption play an important role in these processes, and sorption can also be the key factor controlling the removal of organic pollutants during sewage sludge composting. In the literature, there is no information on the influence of composting on the sorption capacity of hydrophobic organic contaminants in sewage sludges. It is well known that during composting, there are changes in the structure and properties of the organic matter of sewage sludge [16]. The pH and some other physical-chemical properties can change during composting. These can also result in changes in the affinity of the compost matrix to organic contaminants such as PAHs. There is also little information on the organic contaminant forms occurring in sewage sludges [17] or their formation during sewage sludge composting. A connection between the above issues (i.e. bioavailability of contaminants) and contaminants sorption

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capacity is crucial for the understanding of their fate during sewage sludge composting.

The aim of the research studies carried out was to determine: (1) the influence of composting on the changes in the bioaccessible fraction determined by chemical methods; (2) the influence of composting on phenanthrene sorption by sewage sludge; (3) as well as to determine whether changes in the content of the bioaccessible phenanthrene fraction depend on the sorption capacity of phenanthrene by the compost matrix.

2. Materials and methods

2.1. Composting process

Three sewage sludges collected from municipal sewage treatment plants were chosen for the present study. Sewage sludge and composts characteristics as well as conditions of their preparation are presented elsewhere [18,19]. Each sludge was composted in two parallel bins (30 L) for 76 days. The temperature variation during composting followed a typical pattern exhibited by many composting systems. Three phases were observed: (i) the thermophilic phase that lasted until day 12, during which time the temperature rose from 19–22 °C to about 47–55 °C depending on the sewage sludge; (ii) the cooling phase, in which the temperature decreased from 47–55 °C to about 20–23 °C; and (iii) the stable phase with no measurable temperature changes. During the first phase, the pH values decreased (Table 1) as a result of organic acid production. Then, during the remaining two phases, an increase in the pH was noted, most probably resulting from the elimination of organic acids as a result of their degradation together with decomposition of proteins (with ammonia production), which increased the pH values. Mass losses at a level of 15–25% during the first 20 days of composting indicated excellent conditions for bio-oxidation and a high availability of organic matter. During the second and third phases, the daily rate decreased to around 0.2%. These properties show a good biotransformation of initial organic material and that the final compost is stable and mature [19].

Subsamples for analysis (200 g) were collected directly before the onset of the experiment (T0), after 35 (T35) and 76 (T76) days of composting which represented individual phases of the composting process, i.e. the onset (T0), end of the stabilization phase (T35) and end of the maturation phase (T76). Samples for analysis were collected with a stainless steel corer throughout the whole bin height. All samples were air-dried and milled to be representative.

2.2. Sorption experiment

All sorption isotherms were obtained using a batch equilibration technique in screw cap glass vials with aluminum foil–Teflon

liners. The background solution contained 0.01 M CaCl₂ to maintain a constant ionic strength and 200 mg L⁻¹ NaN₃ to minimize biological activity. In the sorption test, 200 mg of sewage sludge or compost was weighed into each 100 mL glass bottle, 90 mL of background solution was added into each bottle. Six concentrations of phenanthrene were used in the sorption test: 0.05, 0.1, 0.18, 0.3, 0.5 and 0.7 mg L⁻¹. The sewage sludge or compost solutions were equilibrated by shaking in a mechanical shaker for 24 h. After equilibration, the bottles were centrifuged at 3000 rpm for 30 min. An amount of supernatant was removed and analyzed for phenanthrene concentrations by HPLC–UV method. All tests were done in triplicate. Controls without sewage sludge or compost but with different concentrations of phenanthrene were prepared at the same time during the sorption test. No significant loss was found in the controls. All sorption data were fitted to the logarithmic form of the Freundlich equation:

$$\log C_s = \log K_F \times n \log C_e$$

where C_s is the solid-phase concentration (mg kg⁻¹) and C_e is the liquid-phase equilibrium concentration (mg mL⁻¹). The parameters K_F for sorption capacity coefficient [(mg kg⁻¹)/(mg mL⁻¹)ⁿ] and n (dimensionless) indicating isotherm non-linearity were determined by linear regression of log-transformed data. The organic carbon-normalized sorption coefficients (K_{oc}) were calculated from K_F ($K_{oc} = K_F/f_{oc}$).

2.3. Determination of phenanthrene in sewage sludge and compost samples

The total phenanthrene content in sewage sludge and compost samples was determined using a method described by Oleszczuk and Baran [20]. The samples (20 g) were extracted in an ultrasonic bath (Sonic-3, Polsonic, Poland) with two batches of dichloromethane (2 × 40 mL). The extract was centrifuged and evaporated. The residue was then dissolved in a mixture 4 mL of acetonitrile:water (1:1, v/v) and purified by solid-phase extraction (SPE) using C18 Octadecyl columns (JT Baker-Mallinckrodt, Germany). An analytical Spherisorb S5 PAH (250 mm × 4.6 mm I.D., 5 μg by Schambeck SFD GmbH, Germany) column was used in presented research. The mobile phase (acetonitrile:water, 82:18, v/v) flow was set to 1 mL min⁻¹. Detection was carried out at 254 nm. The column was installed in a thermostated oven at 31 °C (LCO 101, ECOM, Czech Republic). Data acquisition and analysis was performed using the Clarity Lite Chromatographic Station (DataApex, Czech Republic). All values of phenanthrene were expressed on a dry-weight basis of sample dried for 24 h at a temperature of 105 °C. Phenanthrene determination in sewage sludge or compost samples were carried out triplicate for each sample

Table 1
Changes of some physico-chemical properties during sewage sludges composting

Properties	Sewage sludges (T0, T35) and compost samples (T76)								
	KR			LB			ZM		
	T0	T35	T76	T0	T35	T76	T0	T35	T76
pH	6.1	6.5	6.7	6.5	6.3	5.9	6.9	6.8	6.9
TOC	191.4	183.0	192.6	238.2	231.6	222.0	190.2	164.4	176.4
Na ⁺	32.9	31.8	32.3	27.2	28.5	30.6	28.9	28.6	28.5
K ⁺	32.9	34.6	35.3	44.2	46.1	48.1	57.4	57.3	56.9
Ca ²⁺	446.6	478.2	503.6	311.6	357.8	397.6	325.6	473.3	597.6
Mg ²⁺	128.1	130.1	133.7	177.6	204.3	210.6	176.0	182.7	189.2
CEC	640.5	674.7	704.8	560.7	636.7	686.9	587.9	741.9	872.2
TEB	706.5	731.7	745.3	638.7	741.4	806.9	630.1	779.1	905.2

pH – reactivity in KCl; TOC – total organic carbon (g kg⁻¹); N_t – the total amount of nitrogen (g kg⁻¹); cations – Mg²⁺, Ca²⁺, Na⁺, K⁺ (mmol kg⁻¹); CEC – cation exchange capacity (mmol kg⁻¹), TEB – the total of the exchangeable bases (mmol kg⁻¹). T0, T35, T76 – composting stages (in 0, 35 and 76 day of composting).

and the result was calculated as an arithmetic mean of these determinations.

The method using hydroxypropyl[β]cyclodextrin was adopted from the works of Stokes et al. [21]. The sewage sludges or composts were extracted using an aqueous HPCD shake extraction. Samples (5 g) were weighed into 200-mL Teflon centrifuge tubes and 100 mL of a 50-mM aqueous solution of HPCD was added. The tubes were shaken for 20 h and centrifuged for 30 min. The supernatant was discarded, and the residue sewage sludge was shaken with deionized water and centrifuged again; the supernatant then was discarded. The PAHs content was determined in the residue after extraction with dichloromethane in accordance with the method described above. The differences between the total PAH content (as determined in the dichloromethane) and the residue (after extraction with HPCD) was determined as a HPCD or potentially bioavailable fraction.

The method using mild-solvent extraction with *n*-butanol (BTL) was adopted from the works of Chung and Alexander [22]. Mild-solvent extraction was carried out by the extraction of samples of sewage sludge or compost (15 g) with 80 mL *n*-butanol after which, the extracts were centrifuged and the PAH content was determined in the residue after extraction in accordance with the method described above. The differences between the total PAH content (as determined in the dichloromethane) and the residue (after extraction with *n*-butanol) was determined as an *n*-butanol fraction

2.4. Quality control

For each batch experiment triplicate blank samples (containing only phenanthrene) were prepared and monitored. These blank samples did not indicate any significant phenanthrene degradation or sorptive losses on the glassware for the duration of the experiment. The procedural blank was also determined by going through the same extraction and cleanup procedures for each series of samples. None of the analytical blanks were found to have detectable contamination of the monitoring PAHs, and thus the results were not blank corrected.

The analytical methods were validated in respect to recovery, precision and repeatability, limits of determination, linearity and matrix influences. Recoveries of the phenanthrene from sewage sludges and composts was about 95% and relative standard deviation was 8%. The calculated limit of determination (LOD) was 0.04 mg kg⁻¹ (at an injection sample volume of 20 μ L).

2.5. Physico-chemical properties of sewage sludge and compost samples

The chemical properties of sewage sludges and composts studied were determined by standard methods. The pH was measured potentiometrically in 1 M KCl after 24 h in the liquid/soil ratio of 10 [23] the total of the exchangeable bases (TEB) and cation exchange capacity (CEC) were determined in the 0.1 M HCl

extraction [23]. The total nitrogen (N_t) was determined by the Kjeldahl's method [24] without the application of Dewarda's alloy (Cu–Al–Zn alloy-reducer of nitrites and nitrates). Total forms of cations (Ca^{2+} , Mg^{2+} , Na^+ and K^+) were determined by Pallman methods in 1 M NH_4Cl [25]. Some selected chemical properties of sewage sludge and compost samples have been presented in Table 1.

2.6. Data analysis

A statistical analysis was carried out using Statistica 5.0 software. Statistically significant differences between the results were evaluated on the basis of standard deviation determinations and on the analysis of variance method (ANOVA). The relationships between results were determined by correlation analysis. Significance was set at $P < 0.05$.

3. Results and discussion

3.1. Total phenanthrene content in sewage sludges and changes during composting

The phenanthrene concentration in sewage sludges KR, LB and ZM was, respectively, 169.0 ± 11 , 173.4 ± 11 and $107.0 \pm 9 \mu\text{g kg}^{-1}$ (Table 2). No statistically significant differences were noted in the content of the compound studied between sludges KR and LB. The influence of sludge composting on the content of phenanthrene was varied and depended on the sludge (Table 2; Fig. 1). A significant lowering of its content was noted after 35 days (stabilization phase) in the case of sludges LB and ZM. During this period, the decrease in the phenanthrene content was 32.7% in sludge LB, and 44.4% in sludges ZM. Further composting did not influence this compound content in the above-mentioned sludges in any significant way. In the case of sludge KR, no significant changes in the phenanthrene content during the stabilization phase (up to the 35th composting day) was observed. Whereas, during the maturation phase (from the 35th to the 76th composting day), a significant increase (by 22.4%) in the phenanthrene content was noted as compared to the onset of composting.

3.2. Influence of composting on potentially bioavailable phenanthrene content

The potentially bioavailable phenanthrene content determined by means of BTL and HPCD methods differed depending on the sludge tested from 45.8 to 84.5 $\mu\text{g kg}^{-1}$ and from 8.6 to 84.5 $\mu\text{g kg}^{-1}$, respectively (Table 2). The phenanthrene content in the fraction extracted with BTL was similar in individual sludges (32–48%) (Fig. 2). A higher differentiation was noted in the case of the HPCD method. In sludge KR, the contribution of potentially bioavailable fraction was only 5.1%, whereas in sludges LB and ZM, it remained at a level of 80.3 and 70.9%, respectively. After 35-days of composting (after the stabilization phase), the

Table 2
Changes of different forms of phenanthrene content during composting

Day of composting	Sewage sludges (T0, T35) and compost samples (T76)								
	KR			LB			ZM		
	DCM	BTL	HPCD	DCM	BTL	HPCD	DCM	BTL	HPCD
T0	169.0 \pm 11	54.3 \pm 3	8.6 \pm 1	173.4 \pm 11	84.5 \pm 6	139.2 \pm 12	107.0 \pm 9	45.8 \pm 7	75.8 \pm 8
T35	167.1 \pm 5	91.5 \pm 13	14.4 \pm 1	116.7 \pm 5	82.0 \pm 10	58.1 \pm 4	59.5 \pm 5	7.9 \pm 1	13.0 \pm 1
T76	206.8 \pm 7	103.2 \pm 16	29.1 \pm 3	118.6 \pm 7	77.6 \pm 12	55.1 \pm 5	74.5 \pm 4	24.3 \pm 3	31.3 \pm 3

DCM, BTL and HPCD content of phenanthrene in dichloromethane, *n*-butanol and hydroxypropyl[β]cyclodextrin fraction, respectively. T0, T35, T76 – composting stages (in 0, 35 and 76 day of composting).

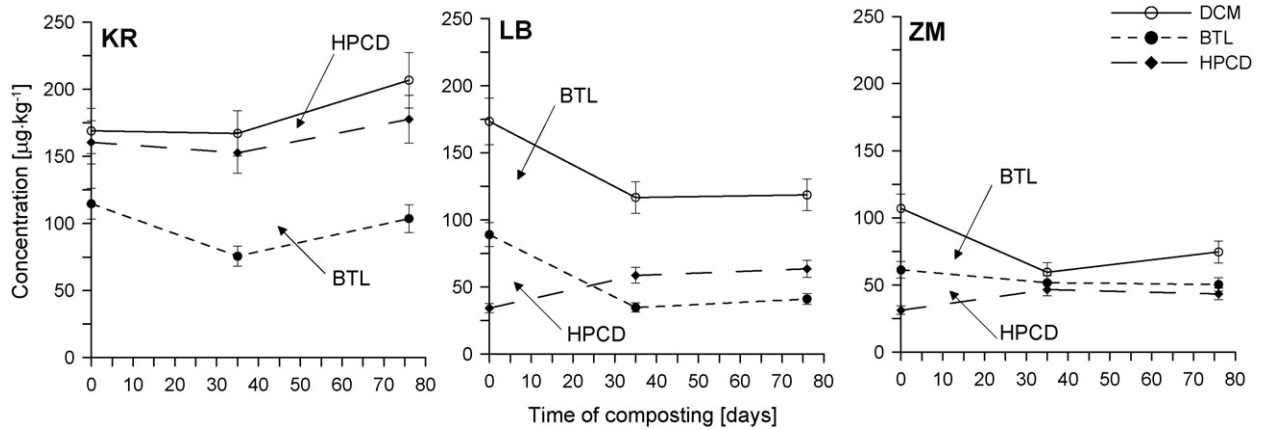


Fig. 1. Changes of phenanthrene content during composting. DCM – extracted by dichloromethane, BTL – extracted by *n*-butanol, HPCD – extracted by hydroxypropyl[β]cyclodextrin. Potentially bioavailable fraction is presented between solid and dashed line.

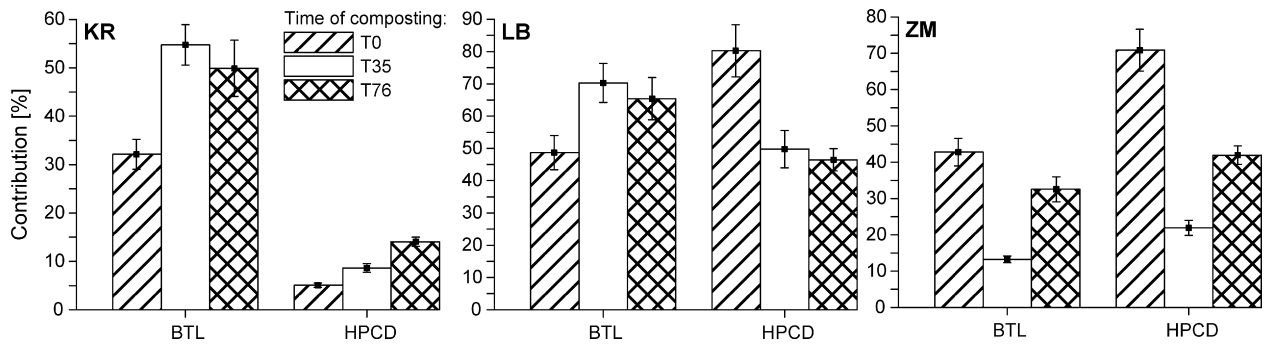


Fig. 2. Changes of phenanthrene contribution in potentially bioavailable PAHs fraction during sewage sludge composting. BTL – extracted by *n*-butanol, HPCD – extracted by hydroxypropyl[β]cyclodextrin, TX – extracted by tenax.

content of the bioavailable fraction (BTL and HPCD) in sludge KR increased, whereas in sludges LB and ZM, it decreased. Sludge LB and its *n*-butanol extracted fraction in the case of which no statistically significant changes were observed, was an exception (Table 2). During the maturation period (from the 35th to the 76th composting day), a further increase in the *n*-butanol and hydroxypropyl[β]cyclodextrin extracted fraction were noted in sludge KR. In sludge LB, during the maturation phase, the potentially bioavailable fraction remained at a constant level. In sludge ZM, an increase in the content of this fraction took place both in the case of the BTL and the HPCD methods (Table 2, Fig. 1).

3.3. Sorption of phenanthrene by sewage sludges

Sorption isotherms of phenanthrene by the sewage sludge or compost are presented in Fig. 3, and the model parameters are summarized in Table 3. Isotherms demonstrated a good fit to the Freundlich isotherm model ($r^2 = 0.92–0.99$). Each of the sewage sludges studied showed a differentiated sorption level in relation to phenanthrene. Sorption coefficients ($\log K_F$) of phenanthrene ranged from 3.42 to 3.98 and decreased in the order of KR > LB > ZM. The $\log K_F$ values were significantly higher than those noted by other authors for soils and sediments [26–28] as well as other organic compounds (oestrone, 17β-estradiol, 17α-ethinylestradiol)

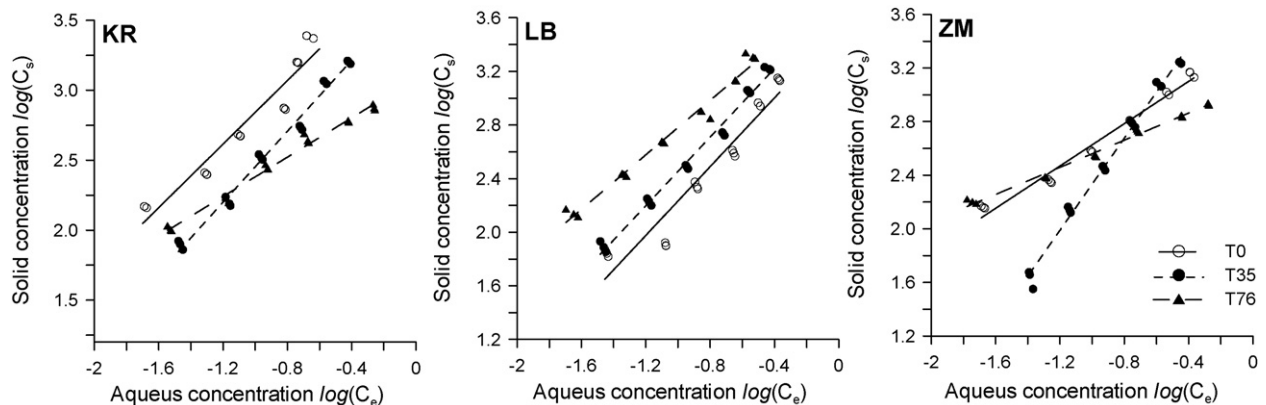


Fig. 3. Adsorption isotherms of phenanthrene onto sewage sludges and composts samples.

Table 3
Freundlich isotherm parameters of phenanthrene for sewage sludge and compost samples in different stages of composting

Properties	Sewage sludges (T0, T35) and compost samples (T76)					
	KR		LB		ZM	
	T0	T76	T0	T35	T76	T76
$\log K_F^a$	3.98 (± 0.01) ^c	3.72 (± 0.04)	3.08 (± 0.01)	3.52 (± 0.03)	3.73 (± 0.01)	3.42 (± 0.01)
n	1.143 (± 0.009) ^c	1.272 (± 0.063)	0.704 (± 0.004)	1.284 (± 0.044)	1.281 (± 0.036)	0.789 (± 0.007)
r^2	0.92	0.99	0.99	0.92	0.99	0.98
N^b	18	18	18	18	18	18
$\log K_{oc}$	4.70	4.46	3.80	4.14	4.37	4.14

^a Units in $(\text{mg kg}^{-1})/(\text{mg L}^{-1})^n$.

^b Number of data points.

^c Standard deviation ($n = 3$). T0, T35, T76 – composting stages in 0, 35 and 76 days of composting.

adsorbed by sewage sludges [29,30]. Sewage sludges exhibited relatively strong affinity for sorption large amounts of phenanthrene like natural organic matter extracted from soil and sediments [31,32] and biopolymers like lignin [33].

In the case of sewage sludge KR and LB the sorption isotherms showed upward curvature ($n > 1$) (Table 3). Observed degrees of non-linear behavior of sorption of organic contaminants by different geosorbents range broadly, with Freundlich n values as low as 0.4 and greater than 1.0 having been variously reported [34]. An upward curvature in the sorption isotherms were noted also for clay minerals and hydrophobic organic contaminants [35,36], biopolymers and PAHs [33], colloidal organic carbon from activated sludge processes and pyrene [37] as well as sewage sludge and endocrine disruptors compounds [29]. Yaron et al. [35] reported an upward curvature of isotherms for aldrin sorbed to Na-montmorillonite. Similarly, an upward curvature for sorption isotherms of phenanthrene by reference smectites (hectorite and montmorillonite) was noted by Hundal et al. [36]. The upward curvature was also observed by Wang et al. [33] for chitin and cellulose samples. The upward curvature of the phenanthrene sorption isotherms suggests that sewage sludge KR and LB possessed some unique sites with strong affinity and capacity to sorb phenanthrene from aqueous solutions. In the case of sludge ZM, a clearly lower value was noted of the n parameter (0.789) than in the case of the two remaining sludges. The sorption isotherms for soils and sediments as well as their organic fraction are typically non-linear ($n < 1$) [31,32,38]. The lower the n value is, the more heterogeneous is the sorption site energy distribution or the higher is the degree of NOM maturation [38]. It suggests that the mechanism of phenanthrene sorption by sludges KR and LB was different than those of the soil/sediment and sewage sludge ZM. Study [39] shows that sewage sludge organic matter is a young organic matter and is significantly different in its chemistry than soil organic matter, which may explain the specific sorption properties of sewage sludges. The organic carbon-normalized sorption coefficient ($\log K_{oc}$) ranged from 4.14 for LB and ZM to 4.70 for KR, which confirmed the strong sorption properties of sewage sludges in relation to phenanthrene. Sorption depends on the physico-chemical properties of the solids and the chemicals involved [38]. Sewage sludge contains metal ions such as K^+ , Ca^{2+} , Mg^{2+} , Cu^{2+} , Zn^{2+} , Fe^{3+} and Na^+ as well as ammonium ions, acetate ions, bicarbonate, fatty acids, lipids and a lot of other contaminants. All of these compounds and components may influence the distribution behavior of the phenanthrene between the solid and the aqueous part of the sewage sludge. Anthropogenic geosorbents (AG) such as sewage sludges most probably possess a broad array of sorption sites due to the differences in their functionality and structure thus demonstrating different energies for HOC sorption.

3.4. Relationships between sorption capacity and bioavailability of phenanthrene

Changes in the individual sorption parameters ($\log K_F$ and n) were closely related to sewage sludge type, and took on various directions (Table 3). In sludge KR, sorption capacity ($\log K_F$) decreased with increases in the composting time as opposed to sludge LB in which an increase in the $\log K_F$ value was noted over time. In sludge ZM, initially there was an increase in adsorption followed by a significant decrease in the $\log K_F$ coefficient value up to a level below the level at the onset of composting in the maturation phase. The values for $\log K_{oc}$ showed a similar pattern (Table 3). Changes in individual parameters were clearly related to the content of the bioavailable fraction as determined by the BTL method as well as HPCD (Fig. 4). The above-mentioned relationship was most clearly visible in KR and LB sewage sludges. The above confirms the assumption from the previous studies [6,18] stating that the sorp-

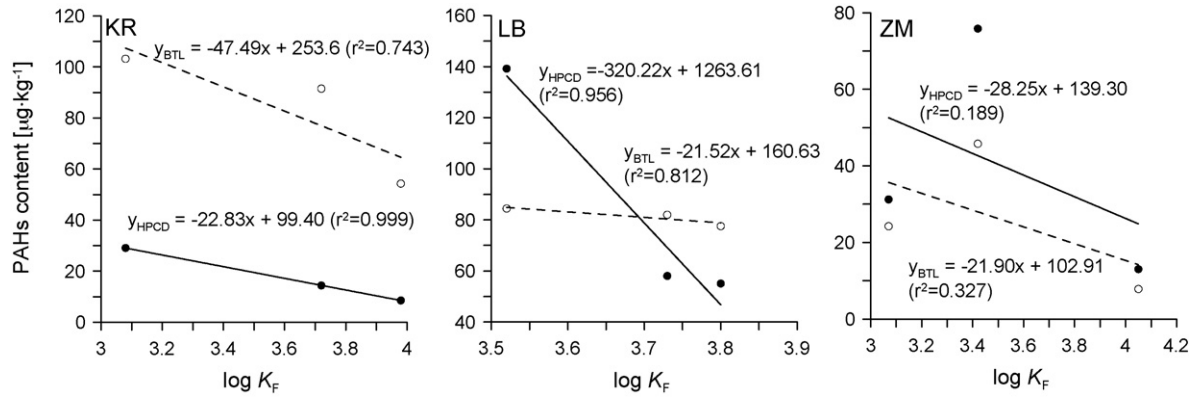


Fig. 4. Relationships between phenanthrene content (bioavailable fraction) and sorption capacity parameter log K_F .

Table 4

The correlations coefficients between changes of sorption parameters and physico-chemical sewage sludge properties during composting

Properties	Sewage sludges and composts samples								
	KR			LB			ZM		
	log K_F	n	log K_{oc}	log K_F	n	log K_{oc}	log K_F	n	log K_{oc}
pH	-0.803	-0.319	-0.956	-0.891	0.946	-0.895	-0.936	-0.975	-0.952
TOC	0.655	-0.921	0.365	-0.926	0.916	-0.929	-0.603	-0.705	-0.641
Na ⁺	0.986	-0.462	0.874	0.915	-0.927	0.918	0.079	-0.057	0.031
K ⁺	-0.829	-0.275	-0.968	0.957	-0.876	0.959	0.639	0.529	0.601
Ca ²⁺	-0.721	-0.437	-0.911	0.972	-0.846	0.974	-0.306	-0.174	-0.259
Mg ²⁺	-0.547	-0.627	-0.795	0.998	-0.651	0.998	-0.344	-0.214	-0.298
CEC	-0.703	-0.460	-0.900	0.987	-0.804	0.988	-0.307	-0.175	-0.261
TEB	-0.791	-0.337	-0.950	0.988	-0.798	0.989	-0.307	-0.175	-0.261

pH – reactivity, TOC – total organic carbon, cations – Mg²⁺, Ca²⁺, Na⁺, K⁺, CEC – cation exchange capacity, TEB – the total of the exchangeable bases.

tion capacity of PAHs by sewage sludge or compost changes during composting and hence influences the increase or decrease in the content of the bioavailable fraction. As suggested earlier [6], it also confirms a possibility of the occurrence of pollutants (which were previously sequestered or unavailable) as a result of a weakening of the influence of the organic pollutants on the compost matrix. HOC sorption depends on the ambient conditions, such as pH, ion strength, temperature, presence of complexing agents or a displacement effect [40,41]. To provide some clues about the mechanisms of phenanthrene interactions with sewage sludge or compost, a correlation analysis was carried out (Table 4). Statistically significant relationships were not noted in any of the cases. However, a clear influence of pH on the change in the solid–water distribution coefficient (log K_F) and organic carbon-normalized distribution coefficient (log K_{oc}) of phenanthrene (Fig. 5) was observed. This

observation is consistent with other reports [42]. The effect of pH is probably due to the increased polarity of the humic material at higher pH as it becomes less protonated. A more polar organic material would have a lower affinity for hydrophobic compounds [43]. A strong relationship between HOC sorption and OC content of soils and sediments has been reported by many researchers but in the present study, only a weak relationship was found between tested coefficients and TOC (Table 4). Some high relationships in the LB sewage sludge were noted in the case of individual cations (K⁺, Na⁺, Ca²⁺ and Mg²⁺), the cation exchange capacity (CEC) and the total of the exchangeable bases (TEB) (Table 4). Exchangeable cations influence mainly the sorption of pesticides and ionic compounds on the solid surfaces [44,45]. However, Hundal et al. [36] observed that sorption capacity of phenanthrene by smectites can also be influenced by the type of cations associated with them. The

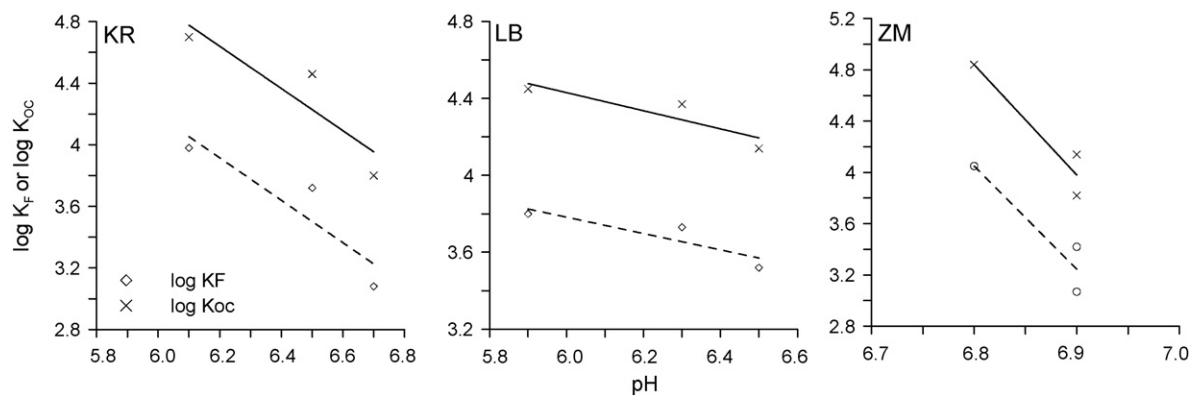


Fig. 5. Relationships between pH and sorption coefficients log K_F and log K_{oc} changes during composting.

Ca-saturated smectites had higher sorption capacities [36] than K- and Na-saturated smectites. In some earlier studies [17], a significant influence of the sorption complex (individual cations and CEC) on the content of the bioavailable fraction was also noted.

Similarly to $\log K_F$ and $\log K_{oc}$, the non-linearity coefficient n underwent changes during composting. However, no relationship between these changes in n and a change in the content of the bioavailable fraction was observed. In the present study, the value of n took on a clearly non-linear character in the case of sludges KR and ZM (Table 3) which was similar to that noted in the case of sorption by organic matter from soils or sediments [28,31,43] and also by black carbon [46]. In the literature [38], the isotherm non-linearity was observed to change as a function of the geochemical characteristics of the soil organic matter associated with the soils and sediments. Hence, it can be assumed that organic matter, when composted, became closer in its properties to the natural organic matter which, in turn, influenced the character of its reactions with phenanthrene. On the last study date in sewage sludge LB a value of the n parameter was close to a linear one (Table 3). Even though, non-linear isotherms of organic compounds by soils and sediments are most often observed, a linear sorption of HOC by soils and sediments was also noted [47]. This suggested that hydrophobic organic contaminants sorption by soil/sediment is highly dependent on the physico-chemical properties (e.g., diagenetic process) of SOM formed in different environmental conditions [48].

4. Conclusion

The aim of the present study was to determine to what degree phenanthrene sorption capacity (measured by means of the sorption method) influences on the content of the bioavailable fraction in the composted sewage sludges. Both the content and changes in the bioaccessible phenanthrene fraction depended on the sewage sludge. It points to some specific properties of sewage sludges which, in turn, requires for each sludge to be treated individually. The sewage sludges and composts studied had a much higher adsorption affinity than natural soils/sediments. An upward curvature also indicates that the phenanthrene sorption mechanism by sewage sludges is different from the soils or sediments. Whereas, the isotherm non-linearity ($n < 0.704$) in composts KR and ZM may suggest that the sorption mechanism resulting from composting becomes similar to that of soils and sediments. The sorption capacity of phenanthrene to sewage sludge varied at individual stages of composting, which significantly controlled the content of the bioavailable fraction of this compound. In the case of two sludges, a strong relationship between phenanthrene sorption capacity and the content of a bioavailable fraction of this compound was noted. Changes in the sorption capacity of phenanthrene resulting from the composted sewage sludge indicated that phenanthrene re-mobilisation may have also occurred. The studies carried out showed that, similarly as in the soils and bottom deposits, sorption determines bioaccessible fraction content to a large degree also in sewage sludges and composts. Hence, for the evaluation of the bioaccessible fraction, it is important to learn which properties of sludges determine sorption capacity. The high PAHs adsorption capacity of sewage sludge and compost indicates their potential environmental risks and significant effect on the fate of PAHs once released to the environment.

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