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Effect of pyrolysis temperature on removal of organic pollutants present in anaerobically stabilized sewage sludge

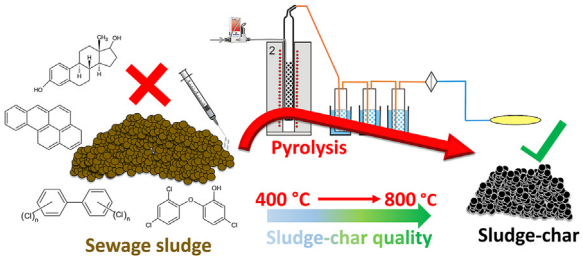
Jaroslav Moško [a, b, c], Michael Pohořelý [a, c, *], Tomáš Cajthaml [d, e], Michal Jeremiáš [a, f], Ana A. Robles-Aguilar [b], Siarhei Skoblia [a], Zdeněk Beňo [a], Petra Innemanová [e], Lucie Linhartová [d, e], Klára Michalíková [d, e], Erik Meers [b]

[a] Department of Power Engineering & Department of Gaseous and Solid Fuels and Air Protection, Faculty of Environmental Technology, University of Chemistry and Technology Prague, Technická 5, 166 28, Prague 6, Czech Republic
[b] Department of Green Chemistry and Technology, Faculty of Bioscience Engineering, Ghent University, Coupure Links 653, 9000, Gent, Belgium
[c] The Czech Academy of Sciences, Institute of Chemical Process Fundamentals, Rozvojová 135, 165 02, Prague 6, Czech Republic
[d] The Czech Academy of Sciences, Institute of Microbiology, Vídeňská 1083, 142 20, Prague 4, Czech Republic
[e] Institute for Environmental Studies, Faculty of Science, Charles University, Benátská 2, 128 01, Prague 2, Czech Republic
[f] The Czech Academy of Sciences, Institute of Plasma Physics, Za Slovankou 1782/3, 182 00, Prague 8, Czech Republic

HIGHLIGHTS

- Fate of four groups of organic micropollutants during sludge pyrolysis was studied.
- Pharmaceuticals were completely removed by pyrolysis.
- 99.8% removal of PCB, PAH, and endocrine-disruptors was achieved by pyrolysis.

GRAPHICAL ABSTRACT



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ABSTRACT

Sewage sludge was excluded from the list of component materials for the production of EU fertilizing products and it was banned as feedstock to produce pyrolysis & gasification materials in European Commission's technical proposals for selected new fertilizing materials under the Regulation 2019/1009 (STRUBIAS report). This exclusion of pyrolysis as a viable way to treat sewage sludge was mainly due to the lack of data on the fate of organic pollutants at pyrolysis conditions. In this work, we are addressing this knowledge gap. We studied slow pyrolysis as a potential process to efficiently treat organic pollutants present in stabilized sewage sludge. Sewage sludge was pyrolyzed in a quartz fixed bed reactor at temperatures of 400–800 °C for 2 h and the sludge and resulting sludge-chars were analyzed for the presence of four groups of organic pollutants, namely (i) polychlorinated biphenyls (PCBs), (ii) polycyclic aromatic hydrocarbons (PAHs), (iii) pharmaceuticals, and (iv) endocrine-disrupting and hormonal compounds. Pyrolysis at ≥ 400 °C effectively removed pharmaceuticals (group iii) to below detection limits, whereas pyrolysis at temperatures higher than 600 °C was required to remove more than 99.8% of the compounds from groups i, ii and iv. Based on these findings, we propose, that high temperature (>600 °C) slow pyrolysis can satisfactory remove organic pollutants from the resulting sludge-char, which could be safely applied as soil improver.

* Corresponding author. Department of Power Engineering, Faculty of Environmental Technology, University of Chemistry and Technology Prague, Technická 5, 166 28, Prague 6, Czech Republic.
E-mail addresses: Michael.Pohorely@vscht.cz, pohorely@icpf.cas.cz (M. Pohořelý).

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1. Introduction

Utilization of sewage sludge by soil application is in accordance with the circular economy principle as it recycles necessary nutrients to the soil. On the other hand, sewage sludge contains pollutants that hinder such use. Heavy metals (or metallic trace elements) are inevitably present in sewage sludge and their content in sewage sludge and sewage sludge based products have been strictly limited in case of soil application (Fijalkowski et al., 2017). Besides heavy metals content of the sludge, the contamination of sewage sludge by organic pollutants is of a significant concern recently, supporting the ban on direct sewage sludge soil application which results in transition to thermal treatment of the sludge, in particular its incineration. Whereas thermal treatment of the sludge can effectively destroy organic pollutants, heavy metals are usually retained in the solid residues (Hartman et al., 2005; Hossain et al., 2011).

Pyrolysis shall be considered as a potential process for treating sewage sludge, especially the sludge with low pollution by heavy metals. Pyrolysis of sewage sludge has been widely studied to produce solid residue (sludge-char) that could be applied to the soil as a fertilizing agent and soil improver with the potential to enhance the soil nutrient content and plant nutrient uptake (Faria et al., 2017; Liu et al., 2014; Sousa and Figueiredo, 2015). The need for reprocessing the sludge-char to fertilizer/soil conditioner is much lower than in the case of sludge incineration ash, and the pyrolysis would also be a viable option for decentralized processing of the sludge compared to large-scale incineration applications. Nevertheless, the STRUBIAS report (one of the first documents considering organic pollutants of various origin for waste-based fertilizing products) questions the efficiency of the removal of organic pollutants by the pyrolysis and gasification processes regarding their contents in products derived from sewage sludge (Huygens et al., 2019). However, this uncertainty comes primarily from the reference to the hydrothermal carbonization (HTC) process, which is a low-temperature process, where the decomposition of the studied pharmaceuticals, pesticides, and industrial chemicals is not complete. Also, some of the substances were observed to be only transformed to other potentially harmful substances (vom Eyser et al., 2016; Weiner et al., 2013).

A broad range of organic pollutants of different origins has been detected in the wastewaters, which inevitably results in the presence of such compounds or their derivates in the sludge of wastewater treatment (Brookman et al., 2018; Carballa et al., 2004; Fijalkowski et al., 2017; Gao et al., 2020; Gomez-Rico et al., 2007; Hamid and Eskicioglu, 2012; Kupper et al., 2004; McClellan and Halden, 2010; Muller et al., 2010; Zhang et al., 2017). Organic contaminants can be of both industrial and domestic origin, usually described as persistent organic pollutants (POPs) and pharmaceuticals and personal care products (PPCPs), which refers to polycyclic aromatic hydrocarbons (PAHs), polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs), polychlorinated biphenyls (PCBs), musk and detergent residues, drugs, hormones and other compounds with endocrine-disrupting potential. It is necessary to note that the concentration ranges of organic pollutants in the sewage sludge are broad due to specifics of the sewage sludge, preferably sludge's differentiation is based on the location and the type of water treated (industrial, municipal, mixed) and the type of the sludge (primary, secondary, raw, digested, etc.). Therefore, concentrations of pollutants differ by an order of magnitudes in the sludge worldwide as may be seen e.g. in Fijalkowski et al. (2017), Gao et al. (2020).

Regarding the agricultural use of the sludge and the fate of various organic pollutants from the groups mentioned above, most of the studies focus on anaerobic digestion of the sludge combined with different pre- and post-digestion treatment techniques (Aemig et al., 2019; Diaz et al., 2020; Gonzalez-Gil et al., 2016; Malmborg and Magner, 2015; Reyes-Contreras et al., 2020; Taboada-Santos et al., 2019; Tomei et al., 2019), showing mostly limited removal efficiency. On the other hand, we hypothesize that pyrolysis will be effective treatment process for the removal of various organic pollutants from the sludge due to high-temperature nature of the process. Temperature is the main parameter influencing the removal and decomposition of the organic matter, including organic pollutants whose thermal stability exceed to a great extent the conditions of conventional sludge treatment processes (except for the incineration).

Since there is a risk of formation of PAHs during the pyrolysis, PAHs are the most studied organic pollutants from the POP group with regards to sewage sludge pyrolysis. Generally, pyrolysis results in lower total USEPA PAH_{16} content (16 PAHs classified as priority pollutants by the United States Environmental Protection Agency) of chars derived from sewage sludge (De la Rosa et al., 2019; Chen et al., 2019; Konczak et al., 2019; Waqas et al., 2014; Waqas et al., 2015; Zielińska and Oleszczuk, 2015) and other types of biomass (Hale et al., 2012) compared to the PAH_{16} content in the feedstock material. Besides that, the increase in the pyrolysis temperature generally results in a decrease in the total USEPA PAH_{16} content of chars, preferably as the result of their transformation to pyrolysis gas (Dai et al., 2014). It has also been studied that pyrolysis generally leads to a decrease in the bioavailable (mobile) fraction of $PAHs_{16}$ (Hale et al., 2012; Zielińska and Oleszczuk, 2016).

In contrast, the effect of pyrolysis temperature on PAH leaching remains unclear as different results have been observed. Whereas Chen et al. (2019) observed the increase in PAHs leaching with an increase in the pyrolysis temperature, Konczak et al. (2019) observed no significant difference in PAHs leaching dependence on pyrolysis temperature. In contrary, Zielińska and Oleszczuk (2016) observed decrease in PAHs leaching from sludge-chars prepared at higher temperatures. The diversity in the results may be the consequence of different methodologies used to determine the leaching and different sludge-char physicochemical properties resulting from pyrolysis of various sewage sludge. Nevertheless, Waqas et al. studied and compared the bioaccumulation of PAHs in tomatoes (Waqas et al., 2015) and cucumbers (Waqas et al., 2014) when sewage sludge and sludge-chars were applied, observing positive effect of the sludge-char amendment, related to reduced bioaccumulation of PAHs compared to control and sewage sludge applied soil. A similar improvement was observed by Khan et al. (2013) in the case of lettuce, suggesting that the application of sludge-char may be a suitable alternative to the direct application of sewage sludge. On the other hand, the studies on the effect of sludge pyrolysis on the removal of other than PAH organic pollutants are scarce. Regarding the pharmaceuticals and the hormones, pyrolysis showed to have a positive effect on the significant removal of triclocarban, triclosan, and nonylphenol (Ross et al., 2016). Similarly, Li et al. (2020) observed complete decomposition of six studied pharmaceuticals during co-pyrolysis of sewage sludge and pig manure at 600 °C. Similarly, pyrolysis was effective in reducing the estrogenicity of the sewage sludge (Hoffman et al., 2016).

Concerning the limited scientific evidence, we studied the effect of pyrolysis on the removal of PCBs, PAHs, pharmaceuticals, hormones and endocrine disruptors. Following the STRUBIAS report, the aim was to tackle the knowledge gap regarding the presence of organic pollutants in sludge-chars which may help to assess the safe use of sludge-chars on the soil as fertilizer/improver.

2. Materials & methods

2.1. Sewage sludge, pyrolysis, and sludge-chars

The studied stabilized sewage sludge was obtained from a wastewater treatment plant (capacity ca 500 000 PE) with mesophilic anaerobic stabilization of the sludge, centrifuge dewatering of the digested sludge, and drying of the dewatered sludge at ca 100 °C for over 3 h. The size fraction of the dried sludge used for the experiments was between 0.5 and 2 mm. The physical and chemical properties of the sludge are summarized in Table 1. Sludge-chars were prepared by slow pyrolysis of approximately 100 g of the sludge in a quartz fixed-bed reactor placed into the electrically heated oven (schematically displayed in Fig. 1) at 400, 500, 600, 700, and 800 °C for 2 h. Sludge-chars are further referred to as SC-XYZ, where XYZ stands for the temperature of the pyrolysis. Helium gas was supplied continuously to the bottom of the reactor at a constant flow rate of 150 ml min^{-1} 30 min before the placement of the reactor into the oven, within the experiment, and during the cooling of the reactor after the experiment. Due to high nitrogen content of the sludge, helium was used instead of nitrogen (often used in laboratory pyrolysis experiments) to be able to balance the mass yield and pyrolysis gas composition more precisely Moško et al. (2020). Considering commercial technologies, the suction fan would be used to extract primary pyrolysis products (condensable vapors and non-condensable gases).

2.2. Analysis of organic pollutants

Representative samples of the sewage sludge and sludge-chars were analyzed for the presence of PCBs, endocrine disruptors, PAHs, and pharmaceuticals and personal care products (PPCPs). The PCBs were analyzed according to Stella et al. (2015). Briefly, the samples were extracted using the Dionex 200 Accelerated Solvent Extraction system (ASE; Palaiseau, France) using a solvent mixture of n-hexane:acetone (1:1, v/v; 100 °C and 13.8 MPa) and analyzed by gas chromatography-mass spectrometry (GC-MS EVOQ; Bruker, MA, USA). The organic extracts were evaporated to dryness, then suspended in n-hexane, treated with a mixture of silica gel/sulfuric acid and applied directly to the chromatography column. The sulfuric acid treatment enables complete removal of the matrix compounds. Therefore, external calibration was used as well as in previous work Stella et al. (2017).

The endocrine disruptors were analyzed according to Kresinova et al. (2018). The samples were extracted with ethyl acetate using the ASE (150 °C and 10.3 MPa) and analyzed by GC-MS EVOQ. The ethyl acetate extracts of endocrine disruptors were purified using gel permeation chromatography (GPC gel BioBeads S-X12; Chromservis, CZ). The fraction containing disruptors was evaporated under the nitrogen stream in the presence of dimethylformamide (100 μl) and trimethylasilylated (using BSTFA; 60 °C; 30 min). The residues of derivatization agent were evaporated, the sample was reconstituted in 800 μl of ethyl acetate and 100 μl of internal standard stock solution (hexachlorobenze in ethyl acetate, 1 mg ml^{-1}) was added before GC/MS analysis. The optimized protocol employing GC-MS enabled the use of external calibration.

The PAHs were analyzed as described previously by Covino et al. (2016). In brief, the samples were extracted with a hexane–acetone (3:1, v/v) mixture using the ASE (150 °C and 10.3 MPa) and analyzed by liquid chromatography with both UV and fluorescent detection (HPLC–FLD). The organic extracts of PAHs were dried under a vacuum at room temperature, dissolved in acetonitrile. PAHs were analyzed using HPLC–FLD. Selectivity of the FLD detectors ensures no matrix interfering compounds were impairing the analyses of PAHs. Therefore, external calibration was used as well as in previous work Čvančarová et al. (2013).

The extraction of PPCPs was performed with methanol using the ASE (80 °C and 10.3 MPa), and the PPCPs were analyzed with liquid chromatography-tandem mass spectrometry (LC-MS/MS). Calibration using standard addition of all PPCPs (three points within the calibration range) to the sample matrix (extract in methanol) was employed (Cimetiere et al., 2013). This approach, together with specific MRM transitions, also ensured the selectivity of the LC-MS/MS method and no additional clean-up was required.

Table 1
Physical and chemical properties of sewage sludge.

W	A^d	V^d	C^d	H^d	N^d	S^d	H/C^d	HHV^d	$pH_{22°C}$	EC	WHC
wt.%							mol mol^{-1}	MJ kg^{-1}	–	μS cm^{-1}	%
9.77	43.3	49.2	28.8	4.20	4.22	1.10	1.75	12.7	6.58	1595	54.4

W – Water (moisture) content, A – Ash, V – Volatiles, C – Carbon, H – Hydrogen, N – Nitrogen, S – Sulfur, H/C – Hydrogen to Carbon molar ratio, HHV – Higher Heating Value, pH – extract at S/L = 1:10 (w/v), EC – Electrical Conductivity (S/L = 1:10 (w/v)), WHC – Water Holding Capacity.
[d] – in dry matter.

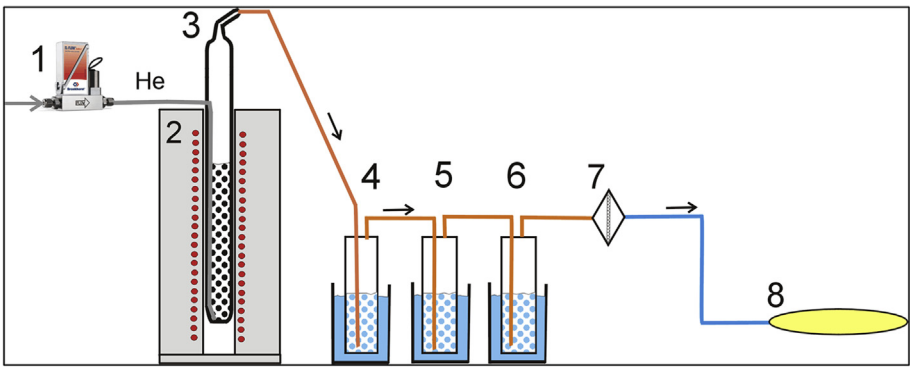

Fig. 1. Scheme of the pyrolysis apparatus: 1 – mass flow controller, 2 – oven, 3 – quartz reactor, 4–6 – ice-water cooled impingers, 7 – porous filter, 8 – Tedlar bag.

The Agilent 1260 Infinity II LC system coupled to the Agilent 6470 LC/TQ mass spectrometer equipped with an Agilent Jet Stream electrospray ion source (Agilent Technologies, Santa Clara, CA, USA) was used for the analysis. The separation of analytes was performed using a CortecsT3 2.7 μm, 3 mm × 150 mm chromatographic column (Waters, USA) with a corresponding security guard. Five μl of the sample was injected. The mobile phases consisted of 1 mM ammonium formate, pH 3 (A) and acetonitrile (B); the flow rate was 0.4 ml min^{-1}. The column temperature was maintained at 40 °C. Gradient elution was as follows (min/%B): 0/10; 4–6/95; 9–11/95; 11.5–15/10. The specific ion transitions were monitored for each analyte in multiple-reaction monitoring mode (MRM) – precursor/quantifier – positive: caffeine 195/138, metoprolol 268/116, carbamazepine 237/194, amitriptyline 278/233, dosulepin 296/223, negative: saccharine 182/106, hydrochlorothiazide 296/269, diclofenac 294/250, ibuprofen 205/161 (The MRM transitions for all the PPCPs are summarized in Table SI1 of supplementary information file - SI). The conditions for electrospray were as follows: drying gas temperature: 200 °C, drying gas flow 9 l min^{-1}, nebulizer pressure: 45 psi, sheath gas temperature: 400 °C, sheath gas flow: 12 l min^{-1}, capillary voltage: +2500 V and −3000 V, nozzle voltage: +0 V and −900 V.

2.3. Removal efficiency

The removal efficiency of pollutants during pyrolysis was calculated according to the following equation:

$$RE = 100 - \left(100 \times \frac{c_{char} \times 0.01 \times Y_{char}}{c_{sludge}}\right)$$

where RE is Removal efficiency in %, c_{char} is the concentration of the pollutant in sludge-char in ng g^{-1} dry matter or μg g^{-1} dry matter, Y_{char} is the yield of sludge-char in wt.% (mass ratio of sludge-char to the sewage sludge feedstock), and c_{sludge} is the concentration of the pollutant in sewage sludge in ng g^{-1} dry matter or μg g^{-1} dry matter.

3. Results and discussion

Pyrolysis of the sewage sludge led to release/decomposition of (primarily) organic matter of the sludge, and an increase in pyrolysis temperature resulted in a decreased yield of the sludge-chars (Y_{char}). The yields were 61.7, 52.9, 50.8, 48.6, and 46.3 wt% for sludge-chars pyrolyzed at 400, 500, 600, 700, and 800 °C, respectively at 2 h residence time for all temperatures under investigation. It was expected that the organic pollutants would be released/decomposed along with the release/decomposition of organic matter of the sludge.

3.1. PCBs

PCBs are a group of 209 congener compounds where from 1 to 10 chlorine atoms substitute the hydrogen(s) atoms of the biphenyl. The number and placement of chlorine atoms determine the toxicity of particular PCBs. Regarding the STRUBIAS report (Huygens et al., 2019), the limit on PCBs maximal concentration has been proposed as 0.8 mg kg^{-1} dry matter (800 ng g^{-1} dry matter) as the sum of 6 congeners (#28, #52, #101, #138, #153, #180 – STRUBIAS PCBs) for pyrolysis and gasification materials.

21 (27) different PCB congeners have been detected either in the sewage sludge or sludge-chars (Table 2), whereas concerning the STRUBIAS report (Huygens et al., 2019) all but #180 congener were detected in the sewage sludge or sludge-chars. Pyrolysis had a positive effect on the removal of PCBs (both STRUBIAS and total). PCBs were surprisingly undetected in SC-400 due to inexplicable reasons. Nevertheless, we observed a significant decrease in PCBs concentration after sewage sludge pyrolysis and with an increase in pyrolysis temperature. The results show that PCBs concentration in all the produced sludge-chars was far below the limit proposed by the STRUBIAS report (Huygens et al., 2019).

Over 97% PCBs RE was achieved by the sludge pyrolysis at 600 °C, followed by RE increase to over 99.8% and over 99.9% for STRUBIAS PCBs and total PCBs, respectively, when the pyrolysis temperature was 700 °C and higher. Regarding the PCBs RE and residual concentration results, it is proposed to run slow sludge

Table 2
Content of detected PCB congeners in sewage sludge and sludge-chars.

PCB congener	sludge		SC-400		SC-500		SC-600		SC-700		SC-800	
	ng g^{-1}	RSD [%]	ng g^{-1}	RSD [%]	ng g^{-1}	RSD [%]	ng g^{-1}	RSD [%]	ng g^{-1}	RSD [%]	ng g^{-1}	RSD [%]
16	5.7	1.5	ND	–	0.6	2.5	ND	–	ND	–	ND	–
22	ND	–	ND	–	0.4	7.1	ND	–	ND	–	ND	–
28 + 31	16.5	0.9	ND	–	0.7	9.9	1.1	15.0	0.3	3.5	ND	–
33	9.7	4.0	ND	–	0.4	26.1	0.6	11.1	ND	–	ND	–
41 + 71	ND	–	ND	–	0.2	7.8	ND	–	ND	–	ND	–
52	28.7	10.8	ND	–	1.0	14.9	2.7	5.5	ND	–	ND	–
66 + 70	8.0	9.1	ND	–	0.5	5.9	ND	–	ND	–	ND	–
72 + 64	ND	–	ND	–	0.2	2.3	ND	–	ND	–	ND	–
74	ND	–	ND	–	0.3	10.1	ND	–	ND	–	ND	–
84 + 92	ND	–	ND	–	0.4	10.5	ND	–	ND	–	ND	–
87	ND	–	ND	–	0.7	11.4	ND	–	ND	–	ND	–
95	ND	–	ND	–	2.3	4.2	ND	–	ND	–	ND	–
101 + 113	4.2	0.5	ND	–	1.0	7.5	ND	–	ND	–	ND	–
110	ND	–	ND	–	1.1	14.6	1.2	7.1	ND	–	ND	–
118	10.1	2.0	ND	–	0.5	6.3	ND	–	ND	–	ND	–
132	93.7	7.0	ND	–	7.2	1.7	3.9	11.7	ND	–	ND	–
138	19.6	14.8	ND	–	0.7	18.9	ND	–	ND	–	ND	–
148	5.0	11.2	ND	–	1.0	10.4	0.6	7.4	ND	–	ND	–
149	26.4	8.4	ND	–	3.9	1.0	2.9	0.2	ND	–	ND	–
153	40.4	7.5	ND	–	2.8	2.0	1.9	2.6	ND	–	ND	–
163	6.1	0.5	ND	–	0.5	2.5	ND	–	ND	–	ND	–
$\sum PCB_{total}$	**274.2**	-	**ND**	-	**26.6**	-	**14.9**	-	**0.3**	-	**ND**	-

ND - not detected.
RSD - relative standard deviation.

Table 3
Contents of detected USEPA PAH_{16} in sewage sludge and sludge-chars.

PAH	sludge		SC-400		SC-500		SC-600		SC-700		SC-800	
	μg g^{-1}	RSD [%]	μg g^{-1}	RSD [%]	μg g^{-1}	RSD [%]	μg g^{-1}	RSD [%]	μg g^{-1}	RSD [%]	μg g^{-1}	RSD [%]
Anthracene	1.57	22.77	0.37	11.95	0.03	25.47	0.02	25.89	ND	–	ND	–
Phenanthrene	4.26	4.47	1.25	28.84	0.07	17.03	0.08	17.88	ND	–	ND	–
Fluoranthene	5.61	7.17	0.69	6.96	0.11	50.22	0.30	11.86	ND	–	0.03	141.42
Benzo[a]anthracene	3.70	0.34	1.53	8.93	0.07	76.43	0.09	17.12	ND	–	ND	–
Chrysene	3.57	2.39	0.93	1.98	0.07	77.41	0.12	22.52	ND	–	ND	–
Pyrene	5.15	7.14	0.87	30.14	0.28	43.05	0.58	9.98	ND	–	0,03	25.43
Benzo[b]fluoranthene	4.68	6.35	1.01	8.75	ND	–	ND	–	ND	–	ND	–
Benzo[k]fluoranthene	2.88	3.80	0.82	15.15	0.04	141.42	ND	–	ND	–	ND	–
Benzo[a]pyrene	4.10	1.00	1.19	2.05	ND	–	ND	–	ND	–	ND	–
∑ PAH	**35.50**	-	**8.67**	-	**0.67**	-	**1.19**	-	**ND**	-	**0.05**	-

ND - not detected.
RSD - relative standard deviation.

pyrolysis at temperatures higher than 600 °C.

The removal of PCBs from the sludge/sludge-char is mainly explained by volatilization to pyrolysis off-gas and decomposition of PCBs during the pyrolysis. Hu et al. (2007) studied the fate of dioxins (PCDD/Fs + PCBs) during pyrolysis of polluted sediments at 800 °C, observing that almost all dioxins were transferred to the volatile phase, and therefore considering the volatilization as the primary mechanism for dioxin removal. To eliminate continued risk, efficient destruction of PCBs is expected after the combustion of the volatile phase of pyrolysis to obtain heat for the process.

3.2. PAHs

PAH specification in sewage sludge and sludge-chars is dependent on the quality of the water treated (concerning PAHs pollution), and the operating conditions of the pyrolysis process (as PAHs can also be formed and adsorbed on the char matrix during the process) (Dai et al., 2014; Hale et al., 2012). Regarding the STRUBIAS report (Huygens et al., 2019), the limit on PAH_{16} maximal concentration has been proposed as 6 mg kg^{-1} dry matter (6 μg g^{-1} dry matter) for pyrolysis and gasification materials.

Out of the sixteen USEPA PAHs tested, nine were detected in the sewage sludge and sludge-chars, respectively, including five out of seven PAHs classified as carcinogenic (benzo[*a*]pyrene, benz[*a*]anthracene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, chrysene, dibenz[*a,h*]anthracene, indeno[*1,2,3-cd*]pyrene) by USEPA (Table 3). All the PAHs detected are from the group of PAHs with 3–5 rings, whereas fluoranthene, pyrene, and benzo[b]fluoranthene were the most abundant in the sewage sludge.

PAH_{16} RE was only 85% for the sludge pyrolysis at 400 °C, resulting in a decrease in the ∑ PAH_{16} concentration from 35.5 μg g^{-1} dry matter in the sludge to 8.675 μg g^{-1} dry matter in SC-400 which is still above the limit proposed by the STRUBIAS report (Huygens et al., 2019). However, a further rise in the temperature resulted in increased PAH_{16} RE (>98% for pyrolysis at ≥ 500 °C), sufficient enough to produce sludge-chars with the ∑ PAH_{16} concentration far below the limit proposed by the STRUBIAS report (Huygens et al., 2019). Most importantly, RE over 99.9% was achieved when sewage sludge was pyrolyzed at 700 and 800 °C, resulting in not detected ∑ PAH_{16} in SC-700 and a concentration of 0.05 μg g^{-1} dry matter in SC-800.

PAHs removal is most likely due to their volatilization to the gaseous phase (boiling point temperatures range from 96.2 to 530 °C) (Dai et al., 2014) and thermal degradation during the pyrolysis process (Zielińska and Oleszczuk, 2015). As a result, it is proposed to pyrolyze sewage sludge over 600 °C with a sufficient residence time in the hot zone (>30 min).

3.3. PPCPs

The sewage sludge and produced sludge-chars were tested for the presence of 27 different compounds from several groups of pharmaceuticals such as antidepressants, stimulants, antipsychotics, anti-inflammatory, analgesics and antibiotics. From all the studied compounds, only nine of them were detected in the sewage sludge; namely amitriptyline, caffeine, carbamazepine, diclofenac, dosulepin, hydrochlorothiazide, ibuprofen, metoprolol, and saccharine, ranging from 0.1 to 50 ng g^{-1} (their concentrations and the list of studied compounds are available in SI file). Pyrolysis had a significant effect on the removal of these compounds, and none of them was detected in the sludge-chars. The results reveal that a pyrolysis temperature as low as 400 °C was sufficient to remove the studied pharmaceuticals below detection limits. Besides hydrochlorothiazide, the boiling points of the compounds are levelling at 400 °C (at a pressure of 760 mmHg), or below (ChemSpider); as a result, it is assumed they either volatilize or decompose.

Further studies to observe the fate of the pharmaceuticals (distribution amongst pyrolysis products) are recommended to prove or disapprove their presence in the liquid products of the pyrolysis, which is beyond the scope of this study. Nevertheless, the destruction of the pharmaceuticals is expected when the combustion of the liquid and gaseous products (volatile phase) of pyrolysis is performed to obtain heat for the pyrolysis process. Regarding the rest of the compounds, since their boiling points are not higher than 600 °C, sewage sludge slow pyrolysis at above 600 °C is proposed to produce safe sludge-chars.

3.4. Endocrine disruptors and hormones

Seven endocrine-disrupting and hormonal compounds were analyzed in the sewage sludge and sludge-chars, namely 4-nonylphenol, bisphenol A, estradiol, estriol, estrone, ethinylestradiol, irgasan (triclosan); however, only bisphenol A, estradiol, and the most abundant irgasan (triclosan) were detected in the sewage sludge in concentrations 1023, 29, and 2236 ng g^{-1} respectively. After pyrolysis (at the whole temperature range studied), only bisphenol A was detected, whose concentration dropped to 5–32 ng g^{-1} in sludge-chars. As pyrolysis temperature increased from 400 to 600 °C, the bisphenol A concentration in sludge-char continuously decreased; however, a further increase in pyrolysis temperature resulted in a slight increase in its concentration for inexplicable reasons. Nevertheless, it should be mentioned that the RSDs (relative standard deviations) were relatively high, exceeding 20% (>60% for SC-400 and SC-800) in the case of bisphenol A analysis in sludge-chars, which may distort the results. Secondly, it may be attributed to the heterogeneity of the sewage sludge, which

was analyzed only once as one representative sample for all pyrolysis experiments.

Overall endocrine-disrupting and hormonal compounds RE by pyrolysis were found to be 99.4% when pyrolysis was operated at 400 °C, which increased to a satisfactory level of over 99.8% at temperatures ≥500 °C. Similarly to PPCPs, their "weak" physicochemical properties (ChemSpider) predetermine endocrine-disrupting and hormonal compounds to volatilize or decompose at elevated temperatures of pyrolysis.

4. Conclusion

Pyrolysis of dry stabilized sewage sludge was performed at 400–800 °C to study the fate of four groups of organic pollutants inevitably present in the sludge – PCBs, PAHs, pharmaceuticals, and endocrine-disrupting and hormonal compounds. Pyrolysis proved to be an efficient process to remove organic pollutants from sewage sludge, especially at the highest pyrolysis temperatures. Pharmaceuticals were effectively removed even at the temperature 400 °C, whereas removal efficiencies for PCBs, PAHs, and endocrine-disrupting and hormonal compounds were exceeding 99.8% when pyrolysis was operated at temperatures over 600 °C. As a result, the final concentrations of PCBs and PAHs in sludge-chars were far below the limits proposed by the STRUBIAS report on pyrolysis and gasification materials. Regarding the organic pollution of sludge-chars prepared by pyrolysis and to be used as a soil improver, slow pyrolysis at high temperature over 600 °C is recommended.

Author contributions

Jaroslav Moško: Validation, Formal analysis, Investigation, Writing – original draft, Visualization. Michael Pohořelý; : Conceptualization, Validation, Resources, Writing – review & editing, Supervision, Project administration, Funding acquisition. Tomáš Cajthaml: Methodology, Validation, Resources, Writing – review & editing. Michal Jeremiáš; : Writing – review & editing. Ana A. Robles-Aguilar: Writing – review & editing, Visualization. Siarhei Skoblia: Methodology, Validation, Formal analysis, Investigation, Resources. Zdeněk Beňo: Methodology, Validation, Formal analysis, Investigation. Petra Innemanová; : Investigation, Resources. Lucie Linhartová; : Validation, Formal analysis, Investigation. Klára Michalíková; : Validation, Formal analysis, Investigation. Erik Meers: Writing – review & editing, Visualization, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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