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PCB CONGENERS OCCURRENCE IN SEWAGE SLUDGE FROM MUNICIPAL WASTEWATER TREATMENT PLANTS IN ROMANIA

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Abstract
Sewage sludges originating from waste water treatment plants (WWTP) act as a sink for various contaminants including polychlorinated biphenyls (PCBs). The fate of organochlorine compounds in sewage sludge is shaped by their physical-chemical properties and by environmental conditions. The high persistence of polychlorobiphenyls (PCBs) in sewage sludge is given by an extremely reduced degradation rate which varies from months to years (the half-life of PCB 28 is 10.9 years, and PCB 52, 11.2 years). Due to their increased hydrophobicity, these carcinogenic compounds can be easily uptake by plants and transferred to the food chain. The present study investigated the occurrence of these seven PCB congeners in sewage sludge sampled from municipal waste water treatment plants from different geographical areas in Romania for a two-year period (2018 and 2019). For the analyzed PCB congeners a database was created concerning their occurrence levels in sewage sludge from these WWTPs. A total number of 62 sewage sludge samples were collected from different WWTPs between 2018-2019 and analyzed for PCB congener content using a validated GC-ECD method according to SR EN 16167/2013. In all the samples that were analyzed in this study the sum of PCB congeners was situated below the maximum allowable concentration (MAC = 0.8 mg/kg d.w.) stated by the Order 708/2004.

Keywords: *PCB congeners, municipal waste water treatment plants, sewage sludge, Romania*

Introduction
Sewage sludge constitutes a threat to the environment due to its utilization in agriculture. As opposed to its useful fertilizing properties, the hydrophobic character of sewage sludge allows adsorption of various pollutants, mainly heavy metals, pathogens and harmful organic compounds (Oleszczuk 2007), which are associated with a potential danger to the environment. The content of PCB congeners in sewage sludge is closely related to the presence of polychlorinated biphenyls in wastewater and it depends on the wastewater type and the share of industrial wastewater and rainwater. The source of PCBs in sewage is mostly liquid waste, e.g., transformer oils or dielectric fluids and run-off from urban catchments, which contain organic substances originating from combustion processes. Due to poor water solubility of PCB, these compounds are prone to adsorption on solid phases like sewage sludge (Gong et al 1998). One of the criteria for assessing the PCB sorption properties is

the hydrophobicity coefficient (log P_{ow}), the more chlorine atoms are in the biphenyl molecule, the greater the log P_{ow} value. The concentration of PCB in sewage sludge can vary over a wide range from trace values up to 10 mg kg^{-1} dry weight (d.w.). The first reports on the occurrence of PCB in sewage sludge came from the United Kingdom in 1942. Investigation on these micropollutants was carried out before it was stated that PCB are compounds noxious to the environment (Wild et al 1990). Since then a lot of data on PCB content in sewage sludge was collected, mainly in Spain (Aparicio et al 2009, Eljarrat et al 2003), Germany (Umlauf et al 2011), Greece (Katsoyiannis & Samara 2011, Mantis et al 2005), Italy (Lazzari et al 2000), Great Britain (Stevens et al 2001), United States (Harrison et al 2006), Australia (Clarke et al 2008) and Poland (Sułkowski & Rosińska 1999). During the sludge stabilization a reduction in organic matter and pathogen organism amount is obtained, and their hydration increases. Biochemical stabilization, aerobic or anaerobic type, is the most frequently used processes. It has been shown that during these processes changes in PCB content in sludge occur, which result from their transformations and lead to reduction in PCB toxicity (Patureau & Trably 2006). Some PCBs called *dioxin-like* congeners are carcinogenic to humans, while others induce neurotoxicity and are endocrine disruptors, and their production is banned (Borja et al. 2005). Despite this, PCB congeners are still identified in environment as secondary products resulted from waste incineration or from industry. The organic contaminants are being removed from soils by physical-chemical technologies or by bioremediation processes which can follow 3 routes: by transferring in other environment compartment (through volatilization, water run-off or by up taking into the plants through the roots), by abiotic degradation processes like oxidation, dehalogenation, dehydrogenation, or by biotic degradation. The hydrophobic nature of PCBs immobilizes the compounds on the soil surface, but organic acids and plant-derived sugars act as a surfactant, which favours the uptake of PCBs into plant tissue or their biodegradation (James et al 2008, Puiu et al 2018). The presence of pesticides in water sources, soil and sewage sludge is becoming a preoccupation in drinking water production, waste water treatment, and water reuse applications due to potential adverse health effects associated with these compounds (Scutariu et al 2018). The application of sewage sludge as a fertilizer for agricultural site can cause health risks by infesting the soil and groundwater with PCBs, heavy metals, pathogens and viruses. These issues have generated a special interest in another elimination alternative, one of which is the combustion of sewage sludge (Serbanescu et al 2018). The present study aims to assess the occurrence and spatial distribution of PCBs in sewage sludge from municipal waste water treatment plants from various locations in Romania. The data on concentration of PCBs in WWTP sewage sludge will be used to show the geographical and temporal distribution of these pollutants in Romania.

Experimental part

Equipments

All analyses were carried out using an Agilent 7890A gas chromatograph with an electron capture detector (GC-ECD). SSL inlet was kept at 280°C and was used in

Pulsed-split mode with a split ratio of 5:1. 1 µL of final extract sample was injected onto a fused-silica capillary column, HP-5MS (60 m, 0.25 mm I.D., 0.25 µm f.d.), coated with 5% phenyl and 95% dimethylsiloxane at a 1.2 mL/min flow-rate (He 6.0). The oven temperature program started from 50°C (held 1 min), increased with 20 °C/min rate to 180°C (held 0.5 min), then increased with 10°C/min to 240°C (held for 4 min), then step-up to 300°C by ramp of 14 °C/min and held 9.5 min. The analytes were monitored by maintaining the ECD detector at 350°C.

Sample preparation

During a two-year period, a number of 30 sewage sludge samples (2018), and respectively 32 sewage sludge samples (2019) were collected from different waste water treatment plants (WWTP) located in Romania. All the samples were analyzed to quantify PCB congeners, namely PCB 28, 52, 101, 118, 138, 153 and 180 using the standardized method described in SR EN 16167/2013.

One of the least found PCB congener (PCB 209) was used as internal standard in the analysis of PCB congeners. The samples were extracted with hexane and acetone; the extracts were dried with anhydrous sodium sulfate. Due to the complex matrix of sewage sludge (numerous interferent hydro and liposoluble chemical compounds), sample clean-up was compulsory. This was achieved by passing 10 mL of sample extract through a purification column (alumina, 3 g). The purification through alumina gave best results, higher recoveries and less interference resulted from the complex organic compound sewage sludge matrix.

Results and discussion

The objective of the present study was to establish the contamination degree with PCB congeners of municipal WWTP sewage sludge from different locations in Romania. In order to accomplish this 30 sewage sludge samples have been analyzed in 2018 and 32 sludge samples in 2019. The investigated municipal waste water treatment plants were from the following cities: Petrobrazi, Satu Mare, Carei, Tulcea, Campulung Muscel, Bucuresti, Vaslui, Botosani, Sf. Gheorghe, Tg. Secuiesc, Calafat, Filiasi, Facai, Carei, Petrosani, Bacau and Arad.

In all the analyzed samples, during 2018 and 2019, the sum of PCB congeners was situated below the maximum allowable concentration (MAC = 0.8 mg/kg d.w.) stated by the Order 708/2004. Despite this, in 2018, some PCB congeners from sewage sludge from waste water treatment plants were above the limit of quantitation (LOQ <0.01 mg/kg d.w.): Petrobrazi-Prahova (PCB 52, 138, 180), Satu Mare (PCB 52, 153), Trusesti-Botosani (PCB 53) and Bucuresti (PCB 153, 180, 138), (Figures 2a, 2b, 2c, 2d). In 2019, values higher than the LOQ (< 0.01 mg/kg d.w.) were recorded for the waste water treatment plants in: Tg. Secuiesc-Covasna (PCB 153), Sf. Gheorghe-Covasna (PCB 180), Bolintin Vale-Arad (PCB 153, 118), Arad (PCB 118, 153, 138, 180), Pecica-Arad (PCB 118, 153, 180), Lipova-Arad (PCB 118, 138, 180), Ineu-Arad (PCB 153) and Bacau areas (PCB 28, 52, 153, 101), (Figures 3a, 3b, 3c, 3d). Results obtained from the monitoring study are presented in the following tables and figures.

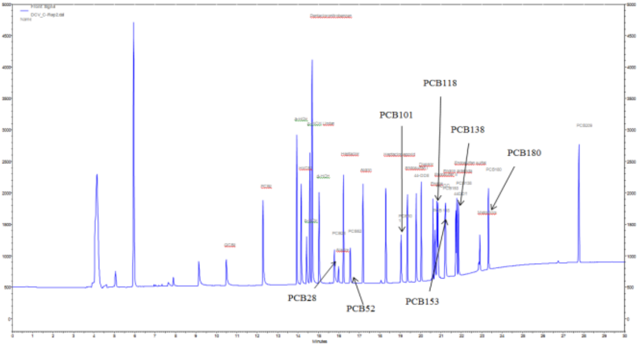


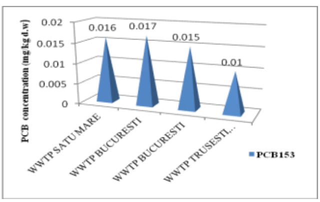
Figure 1. Representative chromatogram of a 10 µg/L PCB congeners standard mixture (PCB 28, 52, 101, 118, 138, 153 and 180).

Table 1. The sum PCB congeners levels in sewage sludge from municipal WWTPs from different locations in Romania in 2018

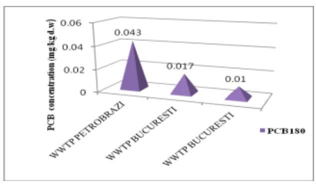
LOCATION	**WWTP PETROBRAZI, PRAHOVA**				
SAMPLE CODE	**PH1**	**PH2**	**PH3**	**PH4**	**PH5**
SUM OF PCBs (mg/kg d.w.)	0.100	<0.01	<0.01	<0.01	0.039
LOCATION	**WWTP VASLUI**				
SAMPLE CODE	**VS1**	**VS2**	**VS3**	**VS4**	**VS5**
SUM OF PCBs (mg/kg d.w.)	<0.01	<0.01	<0.01	<0.01	<0.01
LOCATION	**WWTP BOTOSANI**				
SAMPLE CODE	**BT1**	**BT2**	**BT3**	**BT4**	**BT5**
SUM OF PCBs (mg/kg d.w.)	<0.01	<0.01	<0.01	<0.01	<0.01
LOCATION	**WWTP CRAIOVA**			**WWTP TULCEA**	
SAMPLE CODE	**CR1**	**CR2**	**CR3**	**TL**	**TL**
SUM OF PCBs (mg/kg d.w.)	<0.01	<0.01	<0.01	<0.01	<0.01
LOCATION	**WWTP SATU MARE**			**WWTP SF GHEORGHE**	
SAMPLE CODE	**SM**	**SM**		**SG1**	**SG1**
SUM OF PCBs (mg/kg d.w.)	0.012	0.016		<0.01	<0.01
LOCATION	**WWTP BUCHAREST**			**WWTP CAREI**	**WWTP CONSTANTA**
SAMPLE CODE	**B1**	**B2**		**C1**	**CO**
SUM OF PCBs (mg/kg d.w.)	0.041	0.022		<0.01	<0.01
LOCATION	**WWTP CAMPULUNG MUSCEL**			**WWTP DANUTONI, HUNEDOARA**	
SAMPLE CODE	**CM**			**D1**	
SUM OF PCBs (mg/kg d.w.)	<0.01			<0.01	

Table 2. The sum of PCB congeners levels in sewage sludge from municipal WWTPs from different locations in Romania in 2019

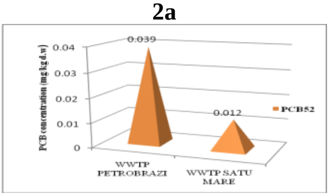
LOCATION	**WWTP BACAU**						
SAMPLE CODE	**BC1**	**BC2**	**BC3**	**BC4**	**BC5**	**BC6**	**BC7**
SUM OF PCBs (mg/kg d.w.)	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
SAMPLE CODE	**BC8**	**BC9**	**BC10**	**BC11**	**BC12**	**BC13**	**BC14**
SUM OF PCBs (mg/kg d.w.)	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
SAMPLE CODE	**BC15**	**BC16**	**BC17**	**BC18**	**BC19**	**BC20**	**BC21**
SUM OF PCBs (mg/kg d.w.)	0.052	<0.01	<0.01	<0.01	<0.01	<0.01	0.021
LOCATION	**WWTP ARAD**		**WWTP INEU**	**WWTP DEZNA**		**WWTP PECICA**	**WWTP LIPOVA**
SAMPLE CODE	**A1**	**A2**	**I**	**D**		**P**	**L**
SUM OF PCBs (mg/kg d.w.)	0.104	0.014	0.015	<0.01		0.055	0.054
LOCATION	**WWTP SANTANA**	**WWTP PANCOTA**	**WWTP BOLINTIN VALE**			**WWTP COVASNA**	
SAMPLE CODE	**S**	**PA**	**BVA**			**TS**	**SG**
SUM OF PCBs (mg/kg d.w.)	<0.01	<0.01	0.094			<0.01	0.060



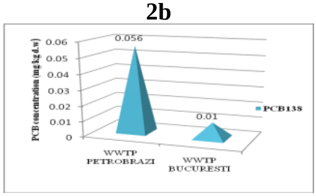
2a



2b

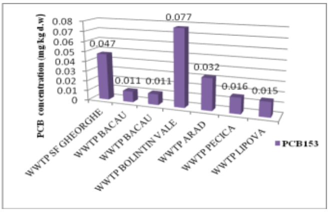


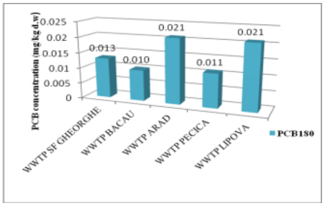
2c



2d

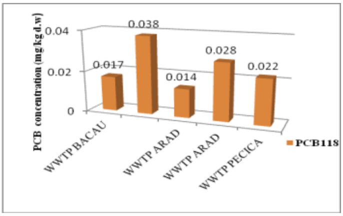
Figure 2. The graphics of the variation during 2018 monitoring study of PCB congeners: PCB 153 (a), PCB 180 (b), PCB 52 (c), and PCB 138 (d), concentrations which are higher than the LOQ method 0.01 mg/kg d.w.

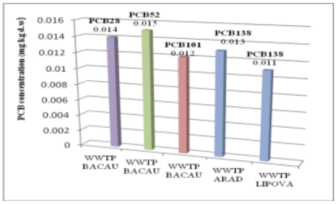




3a

3b





3c

3d

Figure 3. The graphics of the variation during 2018 monitoring study of PCB congeners: PCB 153 (a), PCB 180 (b), PCB 118 (c), PCB 28, PCB 52, PCB 101 and PCB 138 (d), concentrations which are higher than the LOQ method 0.01 mg/kg d.w.

From the available data, PCB 153 was remarked to be the most abundant in contaminated sewage sludge samples (64% in 2019 and 53% in 2018), followed by PCB 118 (45% in 2019), PCB 180 (45% in 2019 an 43% in 2018), PCB 52 (29% in 2018), while the lower chlorinated PCBs as PCB 138 (18% in 2019 and 29% in 2018), PCB 28 and PCB 101 were detected in lower amounts (9% in 2019).

Conclusions

PCBs are a category of highly toxic compounds affecting both human and animal organisms. These pollutants can easily bio accumulate and enter the food chain, due to their persistence in various terrestrial and aquatic ecosystems (soil, water) and due to increased hydrophobicity.

The present study aims to assess the occurrence and spatial distribution of PCBs in sewage sludge from several locations in Romania. In all the samples that were analyzed in this study the sum of PCB congeners was situated below the maximum allowable concentration (MAC = 0.8 mg/kg d.w.) stated by the Order 708/2004. Following the monitoring of sewage sludge from municipal WWTP from different geographical regions in Romania several conclusions can be emphasized.

Although there were no exceedances of the PCB MAC value (0.8 mg/kg) in any of the monitored WWTPs, there were several locations for which PCB congeners were detected in amounts higher than method LOQ (0.01 mg/kg d.w.). The highest values of PCB congeners sum were observed for Petrobrazi (0.100 mg/kg d.w.) and Arad (0.104 mg/kg d.w.) waste water treatment plants. From all available data obtained during the monitoring interval (2018-2019), the PCB 153 congener was remarked to be the most abundant in sewage sludge samples, followed by PCB 118 and PCB 180, while the lower chlorinated PCBs (PCB 28, PCB 52 and PCB 101) were detected in smaller amounts. In 2019, PCB 153 was present in a concentration of 64% in 11 samples with values above the LOQ, PCB 180 in 45%, PCB 118 in 45%, PCB 138 in 18% and PCB 28, PCB 52 and PCB 101 in 9% of the samples. In 2018, in 7 samples analyzed with values above the LOQ were found PCB 153 in 57%, PCB 180 in 43%, PCB 138 and PCB 52 in 29% of the samples. For the rest of the samples which represent a percentage of 71%, there wasn't detected a contamination with article indicated PCBs.

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