ASSESSMENT OF POLYCHLORINATED BIPHENYLS LOAD LEVEL IN SOILS COLLECTED FROM RESIDENTIAL AREAS

Mihaela PREDA, Veronica TĂNASE, Nicoleta Olimpia VRÎNCEANU, Dumitru Marian MOTELICĂ, Vera CARABULEA

National Research and Development Institute for Soil Science, Agrochemistry and Environment, Maraşti 61, 011464, District 1, Bucharest, phone: +40-0213184458, fax: +40-0213184348,
author email: mihaela.preda@icpa.ro

Corresponding author email: veronica.tanase@icpa.ro

Abstract

Polychlorinated biphenyls (PCBs) are listed as a class of Persistent Organic Pollutants (POPs) under the Stockholm Convention. PCBs represent a threat to human health and environment because of their toxicity, persistence, and tendency to bio-accumulate at the top of the food chain. Additionally, some PCBs are suspected carcinogens. Because of their chemical stability and their excellent electrical insulation and thermal conductive properties, PCBs have been used in widespread industrial, commercial and domestic applications. The aim of this study is to establish the load level of these compounds in soils from residential areas. The soil samples were collected from gardens, parks and households located in Bucharest. The interest compounds (PCB with IUPAC number 28, 52, 101, 118, 138, 153, 180) were extracted from soil with organic solvents (hexane: acetone = 1:1) and analysed by gas chromatography with electron capture detector. The analytical results show that the most abundant compounds were those with a high degree of chlorination. The total content of PCBs ranged between 0.0004 mg/kg and 0.028 mg/kg, so values of concentration that are not exceed the alert threshold (0.25 mg/kg).

***Key words**: polychlorinated biphenyls, soil, residential areas*

INTRODUCTION

Polychlorinated biphenyls (PCBs) are synthetic organic chemicals consisting of one to ten chlorine atoms bonded to two phenyl rings that create up to 209 possible congeners. Due to lipophilicity, toxicity, tendency to accumulate in food chains, and low chemical and biological degradation, PCBs have been banned globally under the Stockholm Convention on persistent organic pollutants (POPs). The occurrence of PCBs in remote areas, far from their original sources is thought to be the result of long-range atmospheric transport (Ayris and Harrad, 1999). PCB compounds can now be found in all environmental compartments: sediment, soil, air, water, even in breast milk and fatty deposits of polar bears and whales. PCBs in the environment altered their compositions through various processes such as volatilization and partitioning, chemical or biological transformation, and bioaccumulation. PCBs adsorb strongly to soil, where they tend to persist due to their characteristic properties and, soil acts as a good indicator of pollution and environmental risks (Jones et al., 1991).

Because of their properties, like being nonflammable, highly electrically resistant, with good insulation properties and very stable at high temperatures and pressures, PCBs were first used as dielectric fluids and insulators in transformers and capacitors. In addition to their use for the prevention of fire and explosion, they were used in hydraulic fluids, wax casting, production of carbonless copy paper, compressors, heat transfer systems, plasticizers, paints, adhesives, pesticides, etc. So, the main pollution sources with PCBs are electrical equipment (capacitors and transformers) paint industry, combustion process (municipal

incinerators, gasses from vehicles) but also building materials (Stojic et al., 2014). EPA is concerned that there was potential widespread use of PCB-containing building materials in schools and other buildings constructed or renovated between about 1950 and 1979. Due to their stability and resistance to degradation, PCBs are still present within building construction materials in households and schools and will remain so for centuries to come. For example, in Denmark, 37% of the total housing was constructed in the period when PCBs were used in building materials. PCBs were widely used in caulking and elastic sealant materials, particularly between the 1950s through the 1970s. These materials were primarily used in or around windows, door frames, stairways, building joints, masonry columns, and other masonry building materials.

PCBs were used in these building materials because of their properties as a plasticizer. PCBs have been detected in caulk in buildings, including schools, with concentrations ranging from below 50 parts per million (ppm) to greater than 440 ppm (EPA, 2015).

MATERIALS AND METHODS

The soil samples were collected from 20 points situated in parks and gardens and from 9 households located in Bucharest. They were taken from the topsoil over a 10 m^2 area. Subsamples were combined and carefully homogenized and then an average sample weight of approximately 500 g was taken. A total of five average soil samples were prepared for each sampling area. Samples were collected in all directions. The soil samples were air dried ground and sieved through a < 2 mm sieve before extraction.

10 g of air-dried sample was mixed with anhydrous sodium sulfate, placed in an extraction thimble and Soxhlet extracted for a minimum of 100 extraction cycles with approximately 150 ml acetone/hexane mixture. Acetone is removed with water and the organic extract is reduced to an appropriate volume.

The final extract is injected into a gas chromatograph with the electron-capture detector.

Generally, there is no need for purification of the soil extracts, but if is necessary Florisil is used followed by elution with hexane. Separation and identification of the target compounds (PCB 28, 52, 101, 118, 138, 153, 180) were performed with a non-polar stationary phase capillary column (DB-5MS with 60m x 0.25mm x 0.25μm) with programmed temperature (from 100°C to 330°C with 20°C/minute).

The injector temperature was 250°C and the carrier gas was helium 6.0 at 1ml/min. The injection volume was 1μl in splitless mode. All solvents are high purity grade for chromatography.

Quality control is assured through the use of certified reference material. All samples are analyzed in three replicates and to avoid contamination, a blank is running parallel with the samples.

The blank shall be less than 50% of the lowest reporting limit.

RESULTS AND DISCUSSIONS

The analytical results regarding the PCBs concentration in soils from parks and gardens are presented in Table. 1. The interpretation of the results was done according to Romanian regulations number 756/1997 regarding the content of polychlorinated biphenyls compounds in soils. Thus, the concentration of trichlorobiphenyl (PCB 28), the less chlorinated PCB compound, ranged between 0.0006 mg/kg and 0.0033 mg/kg. It can be observed that all the soil samples are contaminated with this congener. 45% of the soil samples have concentrations of PCB 28 which exceed the normal values (<0.0001 mg/kg), but are lower than the alert threshold (0.002 mg/kg) and 55% exceed the alert threshold. It can be observed that the contribution of PCB 28 at the total concentration is constantly important (figure 1). Similar results regarding the presence of PCB 28 in soil

from urban locations have been reported (Shuai et all, 2018).

Tetrachlorobiphenyl (PCB 52) contaminates only 9 from all the soil samples with concentrations ranging between 0.0004 mg/kg and 0.0018 mg/kg, so values are ten times lower than the alert threshold. This isomer has the lowest contribution to the total content of PCBs. PCB 101 and PCB 118 are pentachlorobiphenyls. Thus, PCB 101 is present in 13 soil samples, the minimum concentration is 0.0006 mg/kg, the maximum value of concentration is 0.0012 mg/kg, so concentrations slightly exceed the normal value.

The same situation can be observed for PCB 118 isomer.

Regarding hexachlorobiphenyls (PCB 138 and PCB 153), these two isomers contaminate all the soil samples. Thus, the concentration of PCB 138 ranged between 0.0006 mg/kg and 0.0028 mg/kg, and for PCB 153 the highest value is 0.0021 mg/kg. Although these values are about ten times lower than the alert threshold, the contribution of these two isomers at the total content of PCBs is important.

PCB 180, a heptachlorobiphenyl isomer, contaminates all the samples and although its concentration is higher than that of the other isomers, it still does not exceed the alert threshold either. In this case, the maximum value of concentration is 0.0057 mg/kg.

Table 1. Polychlorinated byphenyls in soil samples collected from Bucharest parks

Location	Depth	PCB 28	PCB 52	PCB 101	PCB 118	PCB 138	PCB 153	PCB 180	TOTAL PCB
	cm	mg/kg							
Herăstrău	0-10	0,0018				0,0023	0,0005	0,0035	0,0081
Cişmigiu	0-10	0,0010	0,0004	0,0006	0,0016	0,0018	0,0019	0,0020	0,0093
Grădina Icoanei	0-10	0,0027	0,0008	0,0012	0,0021	0,0021	0,0021	0,0020	0,0130
Kiseleff	0-10	0,0032			0,0008	0,0030	0,0011	0,0019	0,0100
Bazilescu	0-10	0,0015				0,0009	0,0009	0,0028	0,0061
Băneasa	0-10	0,0006				0,0012	0,0005	0,0024	0,0047
Plumbuita	0-10	0,0017	0,0014	0,0008	0,0018	0,0019	0,0013	0,0032	0,0121
Drumul Taberei	0-10	0,0022		0,0008	0,0020	0,0028	0,0012	0,0025	0,0115
Andronache	0-10	0,0014		0,0006	0,0006	0,0006	0,0011	0,0018	0,0061
Tineretului	0-10	0,0032	0,0010	0,0010	0,0014	0,0007	0,0009	0,0057	0,0139
Floreasca	0-10	0,0008		0,0006	0,0006	0,0007	0,0007	0,0016	0,0050
Circului	0-10	0,0032		0,0010	0,0018	0,0013	0,0007	0,0017	0,0097
Pantelimon	0-10	0,0028	0,0004	0,0006	0,0022	0,0015	0,0009	0,0017	0,0101
Grădina Botanică	0-10	0,0006			0,0020	0,0014	0,0008	0,0014	0,0062
Bordei	0-10	0,0023	0,0006		0,0012	0,0016	0,0011	0,0015	0,0083
Ioanid	0-10	0,0025	0,0008	0,0006	0,0008	0,0017	0,0009	0,0015	0,0088
Crângaşi	0-10	0,0017	0,0012	0,0008	0,0008	0,0016	0,0007	0,0024	0,0092
IOR	0-10	0,0033	0,0018			0,0013	0,0005	0,0020	0,0089
Izvor	0-10	0,0028		0,0006	0,0012	0,0013	0,0014	0,0012	0,0085
Carol	0-10	0,0030		0,0010	0,0028	0,0015	0,0012	0,0011	0,0106
Normal value		< 0,0001	< 0,0001	< 0,0004	< 0,0004	< 0,0004	< 0,0004	< 0,0004	< 0,0100
Alert threshold		0,002	0,002	0,01	0,01	0,01	0,01	0,01	0,25
Intervention threshold		0,01	0,01	0,04	0,04	0,04	0,04	0,04	1

The presence of highly chlorinated compounds is due to their higher hydrophobicity and affinity for strongly adsorption with soil organic matter (Wilcke et all, 1999). The total content of PCBs ranged between 0.0047 mg/kg and 0.0139 mg/kg. 70% from these values of concentration have normal values (<0.01 mg/kg, 30% exceed the normal values but are ten times lower than the alert threshold (0.25mg/kg). The highest concentrations were reported in Tineretului park, 0.0139 mg/kg, Grădina Icoanei, 0,0130 mg/kg, Plumbuita (0,0121 mg/kg) and Drumul Taberei (0,0115 mg/kg). The reason for this contamination could be the location of sampling areas, namely areas with intense traffic auto. It is well known that the

combution proccess is an important sources for pollution with PCBs. The combustion of fuel from vehicles is one of them. Similar results were reported by Craul and Klein 1980 and Krauss and Wilcke in 2003.

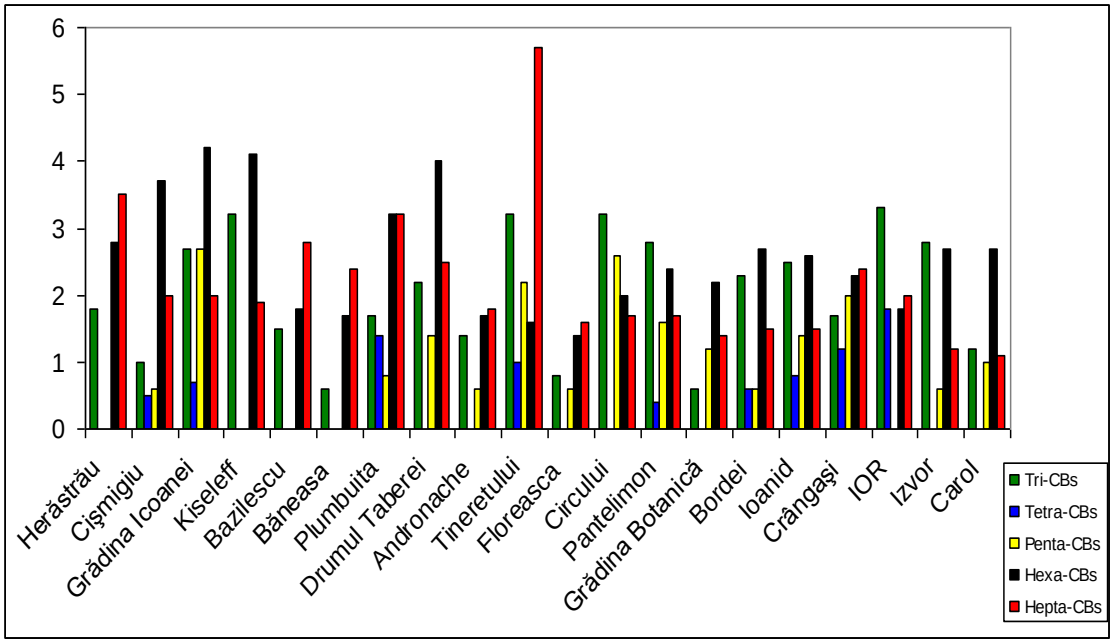

Figure 1. PCB congener profile in soil samples collected from Bucharest parks

The results regarding the content of PCBs in households were presented in Table 2. The soil samples were collected from two depths: 0-10cm and 10-20 cm.

All the soil samples are contaminated especially with highly chlorinated biphenyls (138, 153, 180). Thus, the level of concentration for each isomer is the following: PCB 138: 0.0004 mg/kg – 0.0065 mg/kg, PCB 153: 0.0008 mg/kg – 0.0095 mg/kg, PCB 180: 0.0006 mg/kg – 0.0121 mg/kg. Similar results were obtained by Dimitrova et all, in 2013.

Regarding the less chlorinated isomers (PCB 28, 52, 101, 118) it can be observed that not all the soil samples are contaminated, and the level of concentration is less than the alert threshold.

The total concentration of PCBs ranged between 0.0018 mg/kg and 0.0281 mg/kg, 61% of soil samples have normal concentrations and 39% have concentrations that exceed normal values, but are lower than alert thresholds.

The highest value was reported for P8 Căţelu, where the concentration exceeds even alert threshold (0,25 mg/kg). This contamination could appear because of the combustion of wood pellets used for heating houses. Also, open burning of waste is widely used in our country. This activity is illegal and is connected, as a rule, with ineffective waste collection and removal and their further accumulation (first of all, packaging material). The list of wastes burnt in bonfires is rather large: paper, paperboard, packaging material, polyethylene film, contaminated wood, rags, automobile and tractor tires, plastic bottles, waste food, etc. Often street sweep which contains a great share of domestic wastes is burnt. Spontaneous fires are unavoidable in sanitary landfills of solid wastes and also in places of their unauthorized accumulation (Hedman et al. 2006)

CONCLUSIONS

Soil samples collected from parks are contaminated with PCB, especially with PCB28 and highly chlorinated compounds (PCB 138, 153, 180).

The level of concentration exceeds the alert thresholds in the case of PCB 28 and

it is below this limit in the case of the other isomers.

The soil samples collected from households are contaminated especially with PCB 138, 153, 180. The total content of PCBs ranged from 0.0018 mg/kg and 0.0281 mg/kg, values which exceed the normal values but are ten times lower than the alert threshold.

ACKNOWLEDGEMENTS

This work was funded by the project number 44 PFE /2021, Program 1 – Development of the national research and development system, Subprogram 1.2 – Institutional performance – CDI Excellence Funding Projects

Table 2. Polychlorinated biphenyls in soil samples collected from Bucharest households

Location		Depth (cm)	Content for :							
			PCB 28	PCB 52	PCB 101	PCB 118	PCB 138	PCB 153	PCB 180	TOTAL PCB
			mg/kg							
P1	Străuleşti	0 - 10	0,0014		0,0008	0,0012	0,0030	0,0054	0,0075	0,0159
		10 - 20	0,0006		0,0006	0,0006	0,0027	0,0032	0,0041	0,0100
P2	Străuleşti	0 - 10	0,0008			0,0008	0,0017	0,0011	0,0017	0,0045
		10 - 20			0,0012		0,0026	0,0035	0,0050	0,0111
P3	Roşu (com. Chiajna)	0 - 10	0,0006			0,0014	0,0012	0,0017	0,0018	0,0047
		10 - 20				0,0008	0,0012	0,0015	0,0014	0,0041
P4	Roşu	0 - 10				0,0016	0,0030	0,0034	0,0027	0,0091
		10 - 20					0,0028	0,0030	0,0030	0,0088
P5	Prelungirea Ghencea	0 - 10	0,0012			0,0020	0,0016	0,0015	0,0016	0,0047
		10 - 20	0,0008			0,0008	0,0006	0,0008	0,0010	0,0024
P6	Prelungirea Ghencea	0 - 10				0,0032	0,0032	0,0040	0,0052	0,0124
		10 - 20				0,0012	0,0023	0,0035	0,0045	0,0103
P7	Prelungirea Ferentari	0 - 10	0,0015		0,0008	0,0008	0,0009	0,0015	0,0012	0,0036
		10 - 20					0,0004	0,0008	0,0006	0,0018
P8	Căţelu (sector 3)	0 - 10					0,0065	0,0095	0,0121	0,0281
		10 - 20					0,0032	0,0014	0,0052	0,0098
P9	Căţelu (sector 3) str. Basarabiei	0 - 10	0,0006				0,0022	0,0032	0,0042	0,0096
		10 - 20	0,0006				0,0022	0,0032	0,0043	0,0097
Normal values			*< 0,0001*	*< 0,0001*	*< 0,0004*	*< 0,0004*	*< 0,0004*	*< 0,0004*	*< 0,0004*	*< 0,01*
Alert threshold			*0,002*	*0,002*	*0,01*	*0,01*	*0,01*	*0,01*	*0,01*	*0,25*
Intervention threshold			*0,01*	*0,01*	*0,04*	*0,04*	*0,04*	*0,04*	*0,04*	*1*

REFERENCES

Ayris S., Harrad S., 1999. *The fate and persistence of polychlorinated biphenyls in soil,* Environ. Monit. 1 (4): 395 – 401;

Craul, P.J., Klein J. C., 1980. *Characterization of streetside soils of Syracuse,* N. Y. Metria 3:33-I 01.

Dimitrova A., Stoyanova Y., Tachev A., 2013. *Distribution and risk assessment of polychlorinated biphenyls (PCBs) in urban soils of Sofia City, Bulgaria,* Conference Paper Recent Advances in Chemical Engineering, Biochemistry and Computational Chemistry

Krauss M., Wilcke W., 2003. *Polychlorinated naphthalenes in urban soils: analysis, concentrations, and relation to other persistant organic pollutants*, Environ. Pollut. 122(1): 75-89;

Hedman B., Naslund M., Marklund S, 2006. *Emission of PCDD/F, PCB, and HCB from combustion of firewood and pellets in residential stoves and boillers,* Environ. Sci. Technolog. 40(16):4968-75

Jones K.C., Burnett V., Duarte-Davidson R. and Waterhouse K.S., May **1991**, *PCB's în the Environment*, Chemistry în Britain;

Shuai S., Jianfang X., Yonglong L., Hong Z., Chenchen W., Xianghui C., Qifeng L., 2018. *Are unintentionally produced polychlorinated biphenyl the main source of polychlorinated biphenyl occurrence in soils?* 243 (A): 492-*500.*

Stojic N., Pucarevic M., Mrkajic D., Kecojevic I., 2014. *Transformers as a potential for soil contamination.* Metabk 53(4): 689-692

Wilcke W., Muller S., Kanchanakool N., Niamskul C., Zech W., 1999. *Urban soil contamination in Bangkok: concentrations and patterns of polychlorinated biphenyls (PCBs) in topsoils*, Australian Journal of Soil Research, vol 37, no. 2, pp. 245-254;