POLYCHLORINATED BIPHENYLS IN BUCHAREST URBAN SOILS

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Abstract

Polychlorinated biphenyls are a family of 209 congeners that were manufactured and sold as complex mixtures differing in their chlorination level. They have excellent dielectric properties, chemical and thermal stability, so they were used extensively in industry. PCBs are very persistent, very toxic, and the high octanol/water partition coefficient results in their accumulation in fatty tissues and their biomagnification in the food chain. These are the reasons of including polychlorinated biphenyls on the Persistent Organic Pollutants list adopted in Stockholm in 2001. This paper presents the PCBs (28, 52, 101, 138, 153, 180) load level of Bucharest soils. The samples were collected from representative areas such as parks, streets, intersections, markets. The interest compounds were extracted from soil with organic solvents and analyzed by gas chromatography with electron capture detector. The analythical results show that the most abundant compounds were those with a high degree of chlorination. Thus, for PCB 180, 90% from analyzed samples have concentrations ranged between normal values (< 0.0004 mg/kg) and alert threshold (0.01 mg/kg), 7% between alert and intervention threshold (0.04 mg/kg), while only 3% exceed the intervention threshold. For PCB 153, again, 90% of the values are within the interval normal range – alert threshold and 10% correspond to the interval alert threshold – intervention threshold. For PCB 138, 23% from soil samples have normal concentration, 70% exceed the normal values but are lower than alert threshold, while 7% exceed the alert threshold. The highest concentration value, 0.0542 mg/kg, was recorded for PCB 180 in a sample collected close by a very busy boulevard.

Key words: PCBs, urban soil, gas chromatography.

PCBs (polychlorinated biphenyls) are probably the most studied class of synthetic organic compounds in the environment due to their persistent and wide spread and because it could be responsible for a series of negative effects on life forms, on environment, even at low concentrations.

High chemical stability and electrical resistance, low volatility and resistance to degradation even in the presence of high temperatures led to numerous industrial applications.

Thus, PCBs were used as dielectric fluids in capacitors and transformers, as hydraulic fluids in mining equipment, heat transfer fluid or vacuum pumps, also as plasticizers and additives cement, as lubricating, cutting, and printing inks.

In 1973 it was thought that exist 210 PCB compounds that differ in number and position of chlorine atoms (Jones et al., 1991). Later, the researchers considered theoretical existence of the 209 isomers of PCBs, of which about 150 have been reported in the environment (Larsen and Bowardt , 1993)

PCBs isomers have different toxicities. Thus, non-ortho substituted PCBs (IUPAC no. 77, 81, 126 and 169) belong to the group with the highest toxicity, the mono-ortho substituted (60, 105, 110, 114, 118, 156, 157, 167) are moderate toxic and the remaining 197 are relatively non-toxic (Soniassy et al., 1994). During the last years attention has been focused on the congeners which show the same type of toxicity as polychlorinated dibenzo-p-dioxins (PCDDs) and dibenzofurans (PCDFs). Certain PCBs, which lack chlorine substituents in the ortho-position, show particularly high "dioxine – like" toxicity (PCB 77, PCB 126, PCB 169).

PCBs are extremely persistent compounds. They were first reported in the environment in 1966 by Swedish researchers who studied the presence of organochlorine pesticides in wild birds. Afterwards, other studies showed the presence of traces of PCBs in almost all tested samples collected starting in North America and Europe and reaching to remote areas of the Arctic or Antarctic.

That is the reasons of their including on the Persistent Organic Pollutants (POPs) list, adopted on Stochkolm Convention in 2001, and to which our country has acceded and which require us to monitor these compounds in the environment.

MATERIAL AND METHOD

Bucharest soils are found in natural conditions only in some parks, but most of them are anthropogenic altered soils. Generally are chromic luvisols, luvic phaeozems, haplic chernozems. In the street area and in the vegetable gardens of some suburban zone there are anthropogenic modified soils. In the street area are predominantly anthropogenic protosols.

Physical and chemical characteristics of soils from Bucharest are very different. pH ranges in slightly acid – slightly alkaline and organic matter content, total nitrogen and macroelements contents are different, varying greatly.

For the present study the soil samples were collected from parks, street area and vegetable gardens.

In all samples was analyzed the content of those PCB compounds which are mentioned by the applicable law (Order 756/1997).

- **28** – 2,4,4' - trichlorobifenyl;
- **52** – 2,2',5,5' - tetrachlorobifenyl;
- **101**–2,2',4,5,5' - pentachlorobifenyl;
- **138** – 2,2',3,4,4',5 - hexachlorobifenyl;
- **153** – 2,2',4,4',5,5' - hexachlorobifenyl;
- **180** – 2,2',3,4,4',5,5' - heptachlorobifenyl.

The analythical method for PCBs determination from soil consist of organic solvents extraction, purification and gaz chromatografic determination.

The dried samples are extracted with 50 ml petroleum ether : acetone = 2 : 1. From the etheric extracts were taken 25 ml, which were agitated in the separatory funnel, first with sodium sulphate 2% for removing the acetone and second with 3x25 ml petroleum ether. The extracts were purified on Florisil column, eluted with 6 ml hexan and evaporated to a convenient volume.

The separation of the PCB compounds takes place in a WCOT cappillary column with a non-polar stationary phase (OV 1) and programmed temperature (from 70°C to 330°C with 20°C/minute). The separated compounds are detected with an ECD (electron capture detector) operated at 300°C. The analythical result is a chromatogram were each compund is represented by a peak and a specific retention time. The concentration of each compound is calculated reffering on the calibration curve.

RESULTS AND DISCUSSIONS

A brief examination of the data leads to the conclusion that PCBs 28, compound with three chlorine atoms in the molecule, is undetectable in all samples, while higher chlorinated compounds are present in all samples. It should be noted that where not listed concentrations are below the detection limit *(tab. 1)*.

PCB 52 appears in only five of the 30 samples analyzed with a content which exceed the upper threshold of normal values of 0.0001 mg/kg, and slightly exceed the alert threshold (0.002 mg/kg) only in samples collected from Rosu and Gradina Icoanei.

PCB 101 was found in ten of the thirty soil samples analyzed, and its concentrations slightly exceed the upper threshold of normal values.

PCB 138, the compound with six chlorine atoms in the molecule, is undetectable in areas Rahova and Lujerului. In the other soil samples its concentration varies in the range 0,0002 - 0.0240 mg/kg. The second isomer with six chlorine atoms in the molecule, PCB 153, contaminate all the soil samples and its concentrations was ranged between 0.0005mg/kg and 0.0300 mg/kg. The most polluted samples are collected from Piaţa Rosetti, Piaţa Sudului and Kisseleff (0,5m from the street).

Regarding to PCB 180, the highest chlorinated compound in the study, its content ranged between 0.0004 mg/kg and 0.0542 mg/kg with a maximum in the point Kisseleff at 0.5 meters from the road where the concentration exceeded even the intervention threshold of 0.04 mg/kg. It can be observed higher contents at highly chlorinated isomers, the explanation being that these isomers are more stable and therefore more persistent in soil (Shaw and Connell, 1986).

In conclusion, the contents of PCBs isomers exceed the normal values (<0.0001 mg/kg for PCB 28 and PCB 52 and <0.0004 mg/kg for the other isomers), but are lower than the alert threshold (0.002 mg/kg for PCB 28 and PCB 52 and 0.01 mg/kg for the other isomers). Exceptions are samples collected from Piaţa Sudului, Piaţa Rosetti and Kisseleff street (0.5 m from the road), points where the concentrations exceed even the intervention threshold.

Regarding to the total content of PCBs, the concentrations were ranged between 0.0011 mg/kg and 0.1102 mg/kg, so they are below alert threshold (0.25 mg/kg). It must be emphasized that these values refer only to the sum of concentrations of the six compounds studied. It may be noted that the alert threshold for the total PCBs is much higher than the alert threshold for the six compounds studied, so it covers a wider range of polychlorinated biphenyl isomers.

The highest values were observed in soil samples collected from areas with intens car traffic (Piaţa Rosetti, Piaţa Sudului, şoseaua Kisseleff), where perhaps for many years have accumulated PCBs compounds deposited on the soil mainly from exhaust gases. Following the results obtained from two samples taken near Kisseleff, it can be observed that the content of PCBs in soil strongly decrease (about six times) with increasing distance from the road.

Table 1

Polychlorinated biphenyls in Bucharest soils

	Location	Depth	PCB 28	PCB 52	PCB 101	PCB 138	PCB 153	PCB 180	TOTAL PCB
		cm	mg/kg						
P	Nicolae Bălcescu	0-10					0.0005	0.0009	**0.0014**
A	Cişmigiu	0-10			0.0005	0.0008	0.0019	0.002	**0.0047**
R	Grădina Icoanei	0-10		0.0027	0.0007	0.0021	0.0021	0.002	**0.0069**
C	AAFS	0-10				0.0003	0.0011	0.0009	**0.0023**
K	Tei	0-10				0.0009	0.0009	0.0008	**0.0026**
S	Băneasa	0-10				0.0002	0.0005	0.0004	**0.0011**
	Plumbuita	0-10		0.0015	0.0004	0.0009	0.0013	0.0008	**0.0034**
	Drumul Taberei	0-10				0.0036	0.0024	0.0025	**0.0085**
	Andronache	0-10				0.0006	0.0011	0.0008	**0.0025**
	Băneasa	0-10			0.0007	0.0023	0.0075	0.0074	**0.0179**
M S	Rosetti	5-10			0.0017	0.0152	0.0246	0.0342	**0.0757**
A T	Sudului	0-5			0.0014	0.0078	0.0137	0.0174	**0.0403**
R R	Kisseleff (7m de şosea)	5-10				0.0045	0.0079	0.0079	**0.0203**
K and E	Kisseleff (0,5m de şosea)	5-10			0.002	0.024	0.0300	0.0542	**0.1102**
E E	Dudeşti	0-10				0.0011	0.0023	0.002	**0.0054**
T T	Doamna Ghica	5-10				0.0021	0.0056	0.0072	**0.0149**
S S	Rahova - Antiaeriană	5-10					0.001	0.0015	**0.0025**
	Lujerului	5-10					0.0008	0.0008	**0.0016**
	Ferentari	0-10				0.0004	0.0008	0.0006	**0.0018**
	Progresul	0-10		0.0006	0.0003	0.0007	0.0009	0.0007	**0.0032**
	Lunca Dâmboviţei	0-10				0.0007	0.0007	0.0006	**0.0020**
G	Fundeni	0-10				0.0003	0.0007	0.0007	**0.0017**
A	Pantelimon II	0-10			0.0004	0.0005	0.0009	0.0007	**0.0025**
R	Roşu	0-10		0.0023	0.0006	0.0006	0.0011	0.0005	**0.0028**
D	Domneşti	0-10				0.0007	0.0009	0.0005	**0.0021**
E	Alexandriei	0-10		0.0017		0.0006	0.0007	0.0004	**0.0017**
N	Popeşti Leordeni	0-10				0.0003	0.0005	0.0004	**0.0012**
S	Cătelu I	0-10				0.0008	0.0014	0.0012	**0.0034**
	Pantelimon I	0-10				0.0004	0.0008	0.0007	**0.0019**
	Cătelu II	0-10				0.0005	0.0012	0.0011	**0.0028**
	Normal values		< 0.0001	< 0.0001	< 0.0004	< 0.0004	< 0.0004	< 0.0004	< 0.0100
	Alert threshold		0.002	0.002	0.01	0.01	0.01	0.01	0.25
	Intervention threshold		0.01	0.01	0.04	0.04	0.04	0.04	1

Similar results have been reported (Krauss and Wilcke, 2003) indicating an important decrease in the levels of PCBs in soil at 20 m from street.. Also, near highway Brno the total content of PCBs in soil was 0.3 mg/kg and about0.04 mg/kg at 20 m from this (Crawl and Klein, 1980).

Interpretation of results concerning on the levels of PCBs in soil was done in accordance with the Order of the Ministry of Waters, Forests and Environmental Protection no.756/1997.

Considering all the results it was made a distribution of soil samples concerning their PCBs loading. *(fig. 1)*.

Thus, for PCB 180, 90% from analyzed samples have concentrations ranged between normal values and alert threshold, 7%between alert threshold and intervention threshold, and only 3% exceed the intervention threshold.

For PCB 153, again, 90% from the concentration values are within the interval normal values – alert threshold and 10% correspond to the interval aler threshold – intervention threshold.

For PCB 138, 23% from soil samples have normal concentrations, 70% exceed the normal values but are lower than alert threshold, while 7% exceed the alert threshold.

CONCLUSIONS

In Bucharest all the analyzed soil samples are contaminated with highly chlorinated PCB compounds, ie PCB 138, PCB 153 and PCB 180;

The most polluted areas in the capital are located in areas with intens automobile traffic like Piaţa Rosetti, Piaţa Sudului şi Piaţa Kisseleff, where the concentration exceed even the intervention threshold for sensitive use.

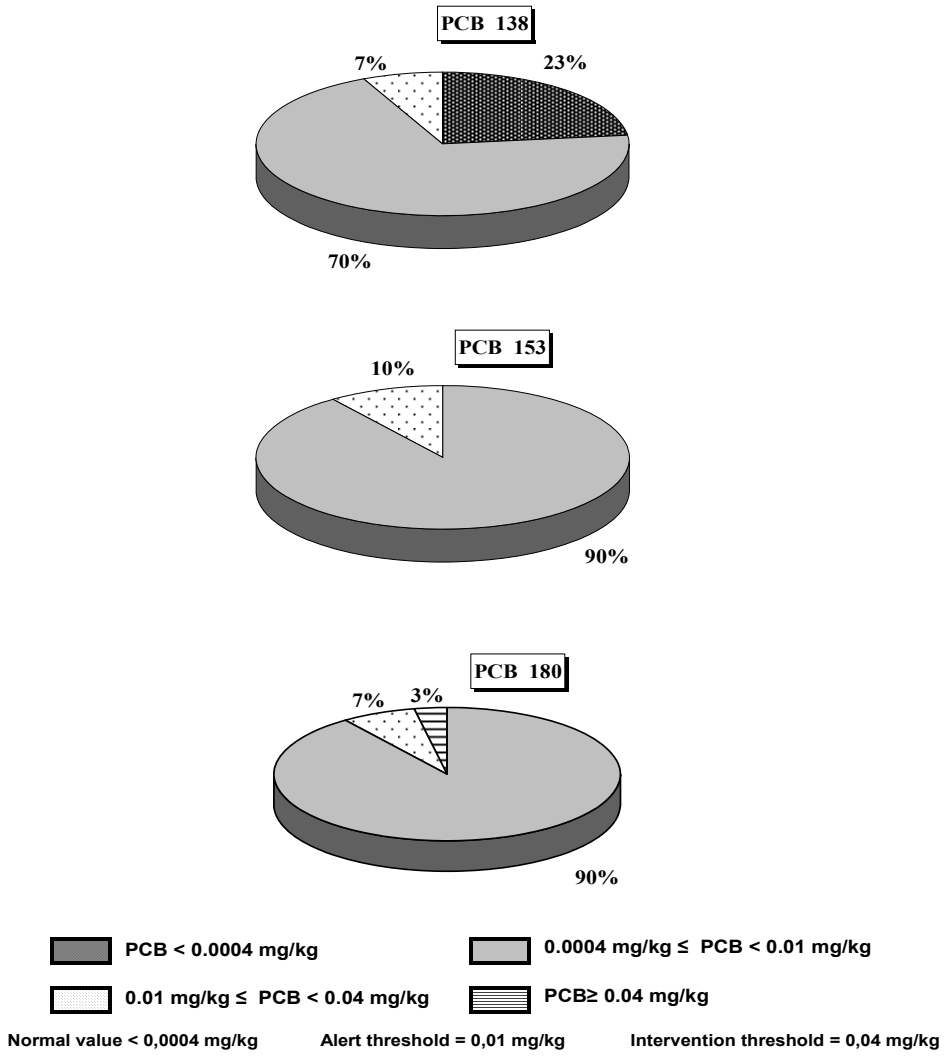

Figure 1 **Distribution of soil samples collected from Bucharest concerning rheir PCBs loading**

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