Scientific Papers, UASVM Bucharest, Series A, Vol. LIV, 2011, ISSN 1222-5339

PERSISTENT ORGANIC POLLUTANTS IN URBAN AND PERIURBAN AREAS

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Keywords: *soil, persistent organic pollutants, chromatography*

Abstract

Persistent organic pollutants are organic compounds that are resistant to environmental degradation through chemical, biological and photolytic processes. Because of this, they have been observed to persist in the environment, to be capable of long-range transport, bioaccumulate in human and animal tissues, biomagnify in food chains, and to have significant impact on human health and the environment. In this study the soil samples are collected from Bucharest and Ilfov county, from representative areas like gardens, parks, industrial zones. The compouds of interes are extracted with solvents and analysed by gas chromatography. The results indicate that organochlorine insecticides still contaminate the samples collected from periurban areas, while PCBs contaminate the soil samples from the center of Bucharest. The concentrations exceed normal values, but are smaller than the alert threshold.

INTRODUCTION

Persistent Organic Pollutants (POPs) are toxic chemicals that adversely affect human health and the environment around the world. Because they can be transported by wind and water, most POPs generated in one country can and do affect people and wildlife far from where they are used and released. They persist for long periods of time in the environment, and can accumulate and pass from one species to another through the food chain. To address this global concern, the United States joined forces with 90 other countries and the European Community to sign a groundbreaking United Nations treaty in Stockholm, Sweden, in May 2001. Under the treaty, known as the Stockholm Convention, countries agreed to reduce or eliminate the production, use, and/or release of 12 key POPs and specified under the Convention a scientific review process that led to the addition of other POPs chemicals of global concern. The 12 key POPs are:

- **8 pesticides**: aldrin, endrin, chlordan, dichlordiphenyl trichlorethane (DDT), dieldrin, heptachlor, mirex, toxafen;
- **2 industrial products**: hexachlorbenzen (HCB), polychlorinated biphenyls (PCBs);

- **2 unintentionally produced substances**: polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs).

Since 2006 hexachlorcyclohexane (HCH) was introduced in the POPs list.

The present study aimed to evaluate the POPs (HCH, DDT and PCBs) load level of some soils collected from representative areas (private gardens, urban zones).

Organochlorine insecticides, namely those based on DDT (pp'-dichlordifenyl-trichlorethane) and HCH (hexachlorcyclohexane) were placed in use in the 40s. They have long been used in crop protection and insect vectors of disease control, about 80% of the amount produced being applied in agriculture.

Technical hexachlorcyclohexane is a combination of isomers containing mainly five isomers in the following proportions: α-HCH (53%–70%), β-HCH (3%–14%), γ-HCH (11%–18%), δ-HCH (6%–10%) and ε-HCH (3%–5%) [3]. γ isomer is the only isomer with strong insecticidal properties and is known as lindane. After nearly forty years of widespread use throughout the world, technical HCH was gradual replaced with lindane. The world has not reported any use of technical HCH since 2000. For lindane, the Regulation on Persistent Organic Pollutants allowed member states to provide exemptions. Thus, until 1 september 2006, lindane could be used in industrial woodworking, construction and industrial applications. Now, both lindane and technical HCH are totally banned in the EU.

DDT was synthesized in 1874 and its pesticide activity was found in 1939 when it was used by the U.S. Army in the Second World War to control typhus, malaria and lice [2]. After the war, DDT was used in agriculture to control insect vectors of disease. For example, in the United States has been much used in cotton crops. So, the main source of DDT pollution is agriculture. In Romania, DDT was produced in one place, namely Borzeşti. Between 1975-1985, DDT was used as an insecticide. Since 1988, DDT-based products were banned in Romania. The DDT metabolites, namely DDD and DDE can be found as a result of metabolic processes that may occur in soil [1]. Monitoring these metabolites in soil is absolutely necessary because they are as toxic as DDT and their persistence may be much higher in soil, as in case of DDE [2].

PCBs have very high chemical stability, high electrical resistance, low volatility and resistance to degradation in the presence of high temperatures. This is the reasons of their many industrial applications. Thus, PCBs were used as dielectric fluids in capacitors and transformers, as plasticizers and additives for cement, as lubricating and cutting oils [4].

MATERIAL AND METHODS

The soil samples were collected from Bucharest (parks, gardens, industrial area) and from the private gardens of Ilfov County. The compounds followed in this study are:

- α, γ, β, δ hexaclorciclohexan;
- pp'-dichlordiphenyl trichlorethan (pp'-DDT) and its isomer op'-dichlordiphenyl trichlorethanul (op'-DDT);
- dichlordiphenyl diclorethan, with two isomers (op'-DDD and pp'-DDD);
- dichlordiphenyl dichlorethene (DDE);
- PCB 28 – 2,4,4' - trichlorobifenyl;
- PCB 52 – 2,2',5,5' - tetrachlorobifenyl;
- PCB 101 – 2,2',4,5,5' - pentachlorobifenyl;
- PCB 138 – 2,2',3,4,4',5 - hexachlorobifenyl;
- PCB 153 – 2,2',4,4',5,5' - hexachlorobifenyl;
- PCB 180 – 2,2',3,4,4',5,5' - heptachlorobifenyl.

The dried samples are extracted with petroleum ether: acetone = 2 : 1. The extracts are purified on Florisil column and evaporated to a convenient volume.1 µl of extract are injected in gaz chromatograf. The separation of POP compounds takes place in a 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 DISCUSSION

The analytical results regarding the content of organochlorine insecticides are presented in Table 1. The total HCH content ranged between 0.002 mg/kg and 0.014 mg/kg, so concentrations slightly exceed normal values (<0.005 mg / kg). As the proportion of isomers, it is noted that in all analyzed samples the isomers β and δ are undetectable, while isomers α and γ contaminate all the samples. Thus, the concentrations of α HCH ranged between 0.0014 mg/kg and 0.0052 mg/kg. These values exceed the upper threshold of normal values (<0.002 mg/kg), but there are about 100 times smaller than the alert threshold (0,1mg/kg). γ isomer have concentrations in the range 0.0003 to 0.0064 mg/kg. In this case the concentrations exceed the upper threshold of normal values (<0.001 mg/kg), but there are about 10 times lower than the alert threshold (0.02 mg/kg).

DDT and its isomers contaminate all the samples. The highest concentrations are observed for isomers pp'DDT and pp'DDE. Thus, for pp'DDE the concentration range between 0.0112 mg/kg in sample collected from Pantelimon and 0.0962 mg/kg in samples taken from Jilava. Practically 50% of the samples have

normal content of DDE and 50% exceed normal values(<0.05 mg/kg), but do not reach the alert threshold (0.25 mg/kg). The total content of DDT is normal in 58% of the analyzed samples, while 42% from samples have concentrations higher than the normal values (<0.15 mg/kg) but lower than the alert threshold (0.5 mg/kg). The highest values of concentration were observed in samples collected from Voluntari.

Table 1

Organochlorine insecticides content in periurban soil

Nr.crt.	*Identification*	*Depth* (cm)	α-HCH	γ-HCH	HCH_{total}	pp'DDE	op'DDD	op'DDD	op'DDT	pp'DDT	DDT_{total}
			mg/kg								
1	Popeşti Leordeni	0-10	0,0014	0,0003	**0,002**	0,0654	0,0016	0,0022	0,0039	0,0033	**0,076**
2		10 - 20	0,0025	0,0049	**0,007**	0,0248	0,0027	0,006	0,006	0,0204	**0,059**
3	Pantelimon	0-10	0,0026	0,0054	**0,008**	0,0273	0,0039	0,0161	0,0201	0,0930	**0,160**
4		10 - 20	0,0026	0,0049	**0,008**	0,0112	0,0028	0,0064	0,0058	0,0241	**0,050**
5	Fundeni	0-10	0,0021	0,0037	**0,006**	0,0380	0,0130	0,0065	0,0078	0,0308	**0,096**
6		10 - 20	0,0027	0,0046	**0,007**	0,0374	0,0187	0,0083	0,0093	0,0381	**0,112**
7	Roşu	0-10	0,0015	0,0032	**0,005**	0,0740	0,0011	0,0028	0,0044	0,0131	**0,095**
8		10 - 20	0,0023	0,0038	**0,006**	0,0256	0,0019	0,0037	0,0055	0,0128	**0,050**
9	Jilava	0-10	0,0031	0,0039	**0,007**	0,0962	0,0031	0,0066	0,0172	0,0481	**0,171**
10		10 - 20	0,0052	0,0092	**0,014**	0,0804	0,0033	0,0125	0,0180	0,0786	**0,193**
11	Voluntari	0-10	0,0043	0,0047	**0,009**	0,0843	0,0101	0,0300	0,0248	0,0929	**0,242**
12		10 - 20	0,0047	0,0064	**0,011**	0,0604	0,0142	0,0401	0,0305	0,1150	**0,260**
normal values			***<0,002***	***<0,001***	***<0,005***	***<0,05***	***<0,05***		***<0,05***		***<0,15***
alert threshold			***0,1***	***0,02***	***0,25***	***0,25***	***0,25***		***0,25***		***0,5***
intervention threshold			***0,2***	***0,05***	***0,5***	***0,5***	***0,5***		***0,5***		***1***

The analytical results regarding the PCBs contents are presented in Table 2. A brief examination of the data leads to the conclusion that PCB 28, the compound with three chlorine atoms in the molecule, is undetectable in all samples, while higher chlorinated compounds are present in all samples. PCB 52 and PCB 101 isomers appear in only one sample with concentrations which exceed normal value (0.0001 mg/kg and 0.0004 mg/kg) but are lower than the alert threshold for the sensitive use (0.002 mg/kg). PCB 138, the compound with six chlorine atoms in the molecule, contaminate all the analyzed soil samples, its concentration ranging between 0.0005 mg/kg in the soil sample collected from a garden located in Voluntari and 0.0095 mg/kg in Piaţa Universităţii.

Table 2

PCBs content in urban soil

Nr.crt.	*Location*	*Identification*	**PCB 28**	**PCB 52**	**PCB 101**	**PCB 153**	**PCB 138**	**PCB 180**	**PCB total**
						mg/kg			
1	**PARKS**	Herăstrău	nd	nd	nd.	0,0021	0,0026	0,0025	**0,0072**
2		Bucureştii Noi	nd	nd	nd.	0,0022	0,0024	0,0012	**0,0058**
3		Crângaşi	nd	nd	nd.	0,0036	0,0026	0,0018	**0,0080**
4		Drumul Taberei	nd	nd	nd.	0,0025	0,0033	0,0027	**0,0085**
5		Cişmigiu	nd	nd	nd.	0,0037	0,0028	0,0026	**0,0091**
6		Carol	nd	nd	nd.	0,0023	0,0030	0,0025	**0,0078**
7		Titan	nd	nd	nd.	0,0033	0,0024	0,0024	**0,0081**
8	**INTERSECTION**	Charles de Gaulle	nd	nd	nd.	0,0023	0,003	0,0025	**0,0078**
9		Victoriei	nd	nd	nd.	0,0070	0,0076	0,0067	**0,0213**
10		Crângaşi	nd	nd	nd.	0,0034	0,0036	0,0039	**0,0109**
11		Lujerului	nd	nd	nd.	0,0028	0,0026	0,0045	**0,0099**
12		Şos. Alexandriei	nd	nd	nd.	0,0044	0,0051	0,0066	**0,0161**
13		Piaţa Sudului	nd	nd	nd.	0,0026	0,0027	0,0032	**0,0085**
14		Grigorescu	nd	nd	nd	0,0027	0,0031	0,0031	**0,0089**
15		Universităţii	nd	0,0010	0,0012	0,0121	0,0095	0,0193	**0,0431**
16		Colentina	nd	nd	nd	0,0033	0,0038	0,0057	**0,0128**
17	**GARDENS**	Popeşti Leordeni	nd	nd	nd	0,0008	0,0010	0,0013	**0,0031**
18		Pantelimon	nd	nd	nd	0,0019	0,0030	0,0022	**0,0071**
19		Fundeni	nd	nd	nd	0,0063	0,0085	0,0120	**0,0268**
20		Roşu	nd	nd	nd	0,0007	0,0008	nd	**0,0015**
21		Jilava	nd	nd	nd	0,0006	0,0008	0,0012	**0,0026**
22		Voluntari	nd	nd	nd	nd	0,0005	nd	**0,0005**
23	**INDUSTRIAL AREAS**	IMGB	nd	nd	nd	0,0022	0,0045	0,0014	**0,0081**
24		Măgurele	nd	nd	nd	0,0024	0,0032	0,0008	**0,0064**
25		Neferal	nd	nd	nd	0,0029	0,0032	0,0022	**0,0083**
26		Faur	nd	nd	nd	0,0025	0,0034	0,0020	**0,0079**
27		Jilava	nd	nd	nd	0,0021	0,0023	0,0018	**0,0062**
normal value			***< 0,0001***	***< 0,0001***	***< 0,0004***	***< 0,0004***	***< 0,0004***	***< 0,0004***	***< 0,0100***
alert threshold			***0,002***	***0,002***	***0,0100***	***0,01***	***0,01***	***0,01***	***0,25***
intervention threshold			***0,01***	***0,01***	***0,04***	***0,04***	***0,04***	***0,04***	***1***

PCB 180, the high chlorinated isomer have concentrations ranged between undetectable and 0.0193 mg/kg. These concentrations exceed the upper threshold of normal (<0.0004 mg/kg), but do not reach the alert threshold (0.01 mg/kg).

The second isomer with six chlorine atoms in the molecule, PCB 153, contaminate all the soil samples studied, except the sample collected from Voluntari. The concentration of this isomer in the soil range from 0.0006 mg/kg and 0.0121 mg/kg. The highest concentration of PCB 153 is observed, again, in the sample collected from Piața Universității, where the content exceeds even the alert threshold. Regarding the highest chlorinated compound content, PCB 180, its concentration range between undetectable and 0.0193 mg/kg. The highest value is observed in the same location, Piața Universității.

CONCLUSIONS

1. Soil samples collected from periurban areas are contaminated with α and γ HCH and DDT (isomers and metabolites).
2. Total concentration of HCH is about 100 times smaller than the alert threshold (0.1 mg/kg).
3. 58% from the analyzed samples have normal content of DDT, while 42% of the analysed soil samples have concentration which exceed the normal values (<0.15 mg/kg) but are smaller than the alert threshold (0.5 mg/kg).
4. The highest value of total PCBs concentration, 0.0431 mg/kg, is observed in the sample collected from Piața Universității. This value exceeds the normal value, but is about ten times lower than the alert threshold.

ACKNOWLEDGEMENTS

Research was supported by Contract C3 bis/2010.

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