STUDIA UBB AMBIENTUM, LXII, 1, 2017, pp. 75-82
(RECOMMENDED CITATION)
DOI:10.24193/subbambientum.2017.1.06

DETERMINATION OF THE CHLORINATED PESTICIDES RESIDUES IN SOILS TREATED WITH MODERN PESTICIDES

Vlad PĂNESCU[1], Pop SORIN[1], Mircea ANTON[1], Mihail Simion BELDEAN-GALEA[1*]

[1] Babeș-Bolyai University, Faculty of Environmental Science and Engineering, Fântânele Street, No. 30, 400294 Cluj-Napoca, Romania;
** Corresponding author: simion.beldean@yahoo.com*

ABSTRACT. The potential for pesticide soil contamination is a worldwide concern, due to the intensive use of organochlorine compounds. The use of pesticides has offered significant economic benefits by increasing the production of food and preventing different form of diseases, therefore their use has affected not only the health of human population, but the environment as well. Organochlorine pesticides like Aldrin, Chlordane, DDT, Dieldrin, Endrin and Heptachlor have been banned after the 2001 Stockholm convention. That is why many jurisdictions try to control human exposure by specifying the soil's maximum allowable concentration. 12 soil samples were collected from different parts of Romania, aiming to evaluate the organochlorine concentration in order to study if the soils have been treated with this type of pesticides. Each sample was dried, extracted with hexane by ultrasonication and analyzed by GC-ECD. The results of the analyzed samples showed low concentrations, ranging between 28.36 and 73.19 µg/kg. The most identified compounds were Alpha HCH, Beta HCH, Heptachlor, Aldrin, Heptaclhor epoxide, trans-Clordane, Endosulfan I, 4,4` DDE and Dieldrin+Endrin.

Key words*: Organochlorine pesticides, modern agriculture, soil*

INTRODUCTION

Organochlorine pesticides (OCPs) are chemical compounds which have been widely used in agriculture for controlling the pests and vector borne diseases (Abhilash and Singh, 2009; Zhang et al., 2011). After the beginning of the 20th century pesticides have been widely spread having traces in all areas of the environment. The use of pesticides has offered the world significant economic benefits by enhancing the production and yield of food and fibers and the prevention of different diseases, evidence suggest that their use has adversely affected the health of human populations and the environment. They are liposoluble compounds and are capable of bioaccumulating in the fatty parts of biota such as breast milk, blood and fatty tissues (William et al., 2008). As a result, human beings are exposed to the effects of these micropollutants by eating foods in contact with contaminated soil or water (Belta et al., 2006; Raposo and Re-Poppi, 2007). These pesticides not only cause

serious diseases in humans but are also highly toxic to most aquatic life (Aiyesanmi and Idowu, 2012) and soil microflora (Megharaj, 2002). They represent the most hazardous class of pesticides. OCPs are very stable compounds and their half-lives can range from a few months to several years in some cases decades (Cremlyn, 1991 cited by Yadav et al., 2015). It has been estimated that the degradation of DDT in soil ranges from 4 to 30 years, while other chlorinated OCPs may remain stable for many years after their use (Afful et al., 2010). OCPs have been used worldwide for over 60 years in different countries around the world. Due to the widespread use of agricultural and residential pesticides, the potential for pesticide soil contamination is a worldwide concern (Cheng et al., 2008). Thus, at least 54 nations have promulgated guidance values to specify the maximum allowable concentration of pesticides in soils. In 2001 under the Stockholm Convention the use of eight OCPs such as aldrin, hexachlorobenzene, chlordane, dieldrin, endrin, heptachlor, mirex, toxaphene) were eliminated because they showed persistence, toxicity and capability of long-range transport. After the Stockholm Convention, many of the organochlorines had been banned and restricted in several countries.

The aim of this study is to evaluate the OCPs concentration in different type of soils treated with modern pesticides in order to evaluate the degree of contamination with these compounds. The study was focused on different regions of Romania.

MATERIAL AND METHODS

Sampling area

The samples were obtained from 12 points from the country, from Transylvania to the southern part of Romania. The sampling points (P1-P12) are presented in the figure 1 and the locations that corresponded to each point are presented in table 1. The samples were obtained from a vegetation-free soil using a shovel to dig about 15 centimeters to avoid getting surface soil that might be contaminated with dust and other suspension particles.

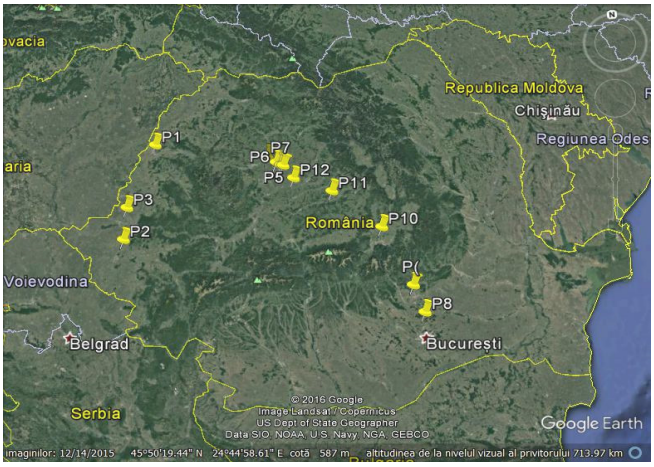

Fig. 1. *The map of the sampling points*

Table 1. *Sampling point and code of the samples made in Google Earth*

Sample cod	Sampling point	County	Coordonates
P1	Oradea, Airport	Bihor	47°1'46.96"N 21°53'37.29"E
P2	Giarmata,	Timiş	45°50'49.98"N 21°18'12.05"E
P3	Arad, entrance from Oradea	Arad	46°14'46.86"N 21°22'27.28"E
P4	Cojocna	Cluj	46°45'12.34"N 23°48'56.63"E
P5	Ceanu Mare	Cluj	46°40'15.79"N 23°57'5.61"E
P6	Valea Largă, entrance from Cluj	Mureş	46°37'50.92"N 24°1'38.14"E
P7	Valea Largă, central	Mureş	46°37'26.17"N 24°3'50.68"E
P8	Săftica, Ilfov	Ilfov	44°37'46.34"N 26°4'13.77"E
P9	Ploieşti, entrance from Braşov	Prahova	44°58'18.51"N 25°56'58.10"E
P10	Braşov, exit to Sighişoara	Brașov	45°43'20.81"N 25°34'39.55"E
P11	Albești, Sighișoara	Mureș	46°14'8.49"N 24°50'3.38"E
P12	Iernut, entrance from Luduș	Mureş	46°26'58.06"N 24°13'2.77"E

Sample processing

Each sample was dried at the room temperature for at least 10 hours. After that, the samples were slowly crushed using a mortar with pestle. 30 grams of the sample were weighted and transferred into an Erlenmeyer flask of 200 mL. The samples were extracted with 40 mL of hexane by ultrasonication for 15 minutes at the room temperature. After decantation, the supernatant was removed, filtered through a PVDF sample filter with pore size of 0.45 μm (Merck Milipore) and evaporated to dryness at the room temperature. Subsequent the residue was redisolved in 2 mL hexane and analyzed by GC-ECD under the conditions described below.

Analysis conditions

Analysis of OCPs was performed using a Thermo Trace Focus GC gas chromatograph equipped with an electron capture detector (ECD) (Thermo Electron Corporation). Nitrogen of high purity at a constant flow rate of 2 mL min^{-1} was used

as carrier gas. The inlet temperature was set at 320 ºC and the injection was made in splitless mode. The temperature of ECD detector was set at 320°C and the auxiliary gas (nitrogen) was set at 40 mL min^{-1}.

For the separation of the tested compounds a TRB-35 column (30 x 0.25 mm, 0.25 µm film thickness) purchased from Teknokroma, Spain was used. The separation of compounds was performed with a gradient temperature program, starting by heating of 15ºC min^{-1} from 180ºC to 250ºC, and from 250ºC to 320ºC, 3ºC min^{-1}, 5 minutes final hold time.

The data acquisition was performed using the Chrom-Card software. The identification of the compounds was done based on the retention time of a standard mixture of 20 OCPs, purchased from Restek. The chromatogram of the tested compounds is presented in figure 2.

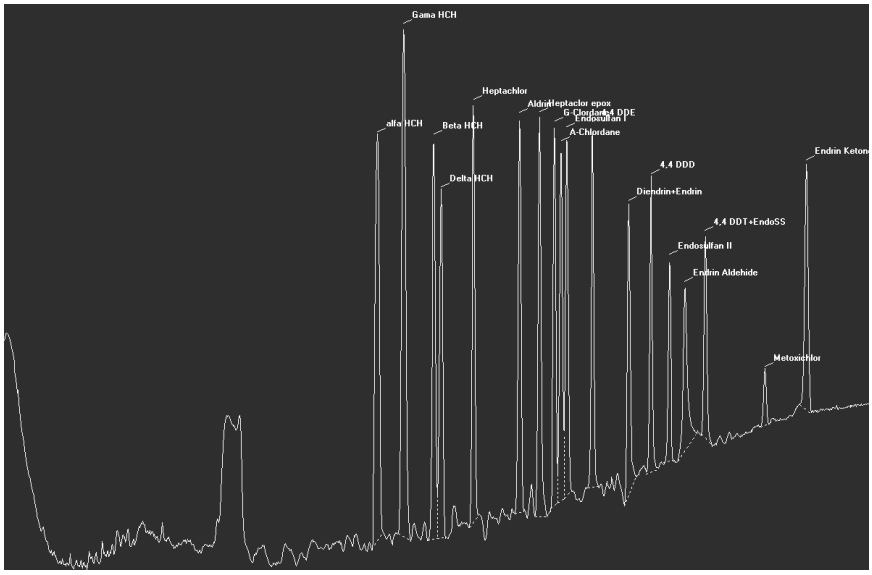

Fig. 2. *The chromatogram of a standard mixture in concentration of 0.2 ppm*

RESULTS AND DISCUSSIONS

The analysis of the target compounds were performed using the method described above. The performances of the optimized method are presented in the table 2.

As can be seen in table 2 the method has a good linearity, repeatability and a limit of quantification able to quantify the compounds at the concentration level expected in the real soil samples. Thus, the method can be applied for the analysis of real soil sample.

Table 2. *The performance of the optimized GC-ECD method*

Compounds	Calibration curve equations	Correlation coefficients	Repeatability RSD %	LOQs mg kg^{-1}
Alpha HCH	y = 2E+06x + 165438	1	0.42	0.90
Gamma HCH	y = 2E+06x + 22938	0.996	0.76	1.29
Beta HCH	y = 2E+06x + 49276	0.9297	2.39	1.94
Delta HCH	y = 1E+06x + 86323	0.9325	1.18	1.42
Heptachlor	y = 1E+06x + 287363	0.9971	7.01	1.79
Aldrin	y = 2E+06x - 114664	0.9624	5.27	1.81
Heptaclor epoxide	y = 2E+06x + 87527	0.9564	4.06	1.28
trans-Chlordane	y = 1E+06x + 101095	0.94	5.43	1.51
cis-Chlordane	y = 899744x + 163458	0.9725	0.77	1.81
Endosulfan I	y = 985702x + 97260	0.9502	6.06	1.94
4,4` DDE	y = 1E+06x + 109135	0.9079	7.77	1.80
Dieldrin+Endrin	y = 2E+06x - 25722	0.9543	5.60	2.46
4,4` DDD	y = 1E+06x + 48338	0.9996	1.27	2.15
Endosulfan II	y = 671002x + 6225,5	0.9948	6.89	2.71
Endrin Aldehide	y = 388136x + 65817	0.9132	9.53	2.85
4,4` DDT+EndoSS	y = 742300x + 33344	0.9915	1.56	2.75
Metoxichlor	y = 175739x + 6111	0.9574	1.43	2.56
Endrin Ketone	y = 1E+06x + 28014	0.9885	1.99	3.25

The results of the analyzed soil samples showed that the concentrations of OCPs are low varying between 28.36 and 73.19 μg kg^{-1} (table 3). A total of 20 OCPs were identified with concentration varying in the range of not detected to few micrograms per kilogram soil. The highest concentrations were detected in the areas near Cluj-Napoca (P4, P5) and Târgu-Mures (P10, P12), meaning that in these areas OCPs were widely used in the past for agriculture. The lowest detected concentration was in sample P1, sample collected near Oradea, Bihor County. On the other hand, the highest concentration was found in sample P10, collected near Iernut, Mureş County which has a long history in the cultivation of industrial plants. The most identified OCPs were Alpha HCH, Beta HCH, Heptachlor, Aldrin, Heptaclhor epoxide, trans-Clordane, Endosulfan I, 4,4` DDE and Dieldrin+Endrin.

The most prevalence of alpha-HCH isomer may lead to the conclusion that technical HCH (60–70% alpha-HCH, 5–12% beta-HCH and 10–12% gamma-HCH), was used in agricultural practices in the majority of locations instead of pure lindane (gamma-HCH). Moreover high incidence of 4,4` DDE instead of 4,4` DDD and 4,4` DDT may suggest that it originated from old usage of this insecticide in agriculture (Ene et al., 2012).

By comparing the obtained data with the reference values for traces of chemical elements in soils (O.M. No. 756/03.11.1997) it can be observed that the only Alpha HCH and Beta HCH concentrations exceed the normal values stipulated by legislation. For Heptachlor, Chlordane, 4,4` DDE, 4,4` DDD and 4,4` DDT the concentrations are very low or not detected.

Table 3. *The concentrations of OCPs in the analyzed soil samples*

Compounds	Concentration (µg kg^{-1} dry soil)													
	P1	P2	P3	P4	P5	P6	P7	P8	P9	P10	P11	P12	NV	AL
Alpha HCH	2.96	nd	3.07	3.44	3.53	3.83	4.19	3.91	3.50	4.14	7.32	1.01	<2	100
Gamma HCH	nd	1.64	nd	nd	1.27	nd	1.02	nd	nd	nd	1.23	nd	<0.1	50
Beta HCH	4.14	1.83	3.57	3.91	7.25	3.00	6.24	8.67	4.12	4.28	8.40	4.16	<1	20
Delta HCH	nd	nd	nd	nd	2.82	nd	nd	3.18	nd	nd	3.19	8.11	-	-
Heptachlor	nd	14.90	7.24	1.75	8.47	5.15	1.79	1.89	11.79	10.89	nd	nd	-	-
Aldrin	2.38	2.87	1.13	5.51	9.51	2.62	3.75	3.02	3.38	3.24	3.01	16.10	-	-
Heptaclor epoxide	4.75	5.30	5.99	5.93	6.75	5.00	6.29	7.49	6.00	7.37	7.28	2.26	-	-
trans-Chlordane	4.51	5.57	5.75	6.90	5.33	4.57	6.17	6.89	6.03	7.72	6.68	7.74	-	-
cis-Chlordane	1.19	4.65	3.74	nd	nd	nd	nd	nd	nd	5.58	nd	10.55	-	-
Endosulfan I	nd	nd	1.21	8.74	2.37	2.59	2.01	2.11	2.27	2.24	1.80	9.72	-	-
4,4` DDE	nd	nd	1.13	6.04	1.14	1.23	1.91	1.60	nd	1.54	2.00	2.95	<50	500
Dieldrin+Endrin	7.15	6.84	7.76	5.27	8.11	7.26	8.51	nd	8.39	nd	14.37	1.71	-	
4,4` DDD	nd	nd	nd	3.87	nd	nd	nd	1.31	nd	nd	nd	3.11	<50	500
Endosulfan II	nd	nd	nd	nd	nd	nd	nd	1.34	nd	nd	nd	2.73	-	-
Endrin Aldehide	nd	nd	1.14	2.39	1.81	nd	nd	4.02	nd	nd	nd	nd	-	-
4,4` DDT+EndoS	nd	1.29	nd	nd	nd	2.36	nd	nd	nd	nd	nd	1.98	<50	500
Metoxichlor	1.29	1.38	nd	1.09	nd	nd	nd	1.57	1.76	2.31	3.85	1.06	-	-
Endrin Ketone	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	P12sigh	nd	-	-
Total OCPs	28.37	46.27	41.72	54.83	58.37	37.59	41.88	47.01	47.25	49.30	7.32	73.19	-	-

nd- not detected, NV-normal value, AL – alert level established by O.M. No. 756/03.11.1997

CONCLUSIONS

The results of the performed studies shows that in all sampling sites the concentration of OCPs are low and do not exceed the alert level and intervention threshold in the sensitive (agricultural/residential) area.

These concentrations are the results of their use in the past and not in this time.

The prevalence of alpha-HCH isomer may lead to the conclusion that technical HCH was used in agricultural practices in the majority of locations instead of pure gamma-HCH.

High incidence of 4,4` DDE instead of 4,4` DDD and 4,4` DDT may suggest that it originated from old usage of this insecticide in agriculture.

Acknowledgements

The authors thanks to the Faculty of Environmental Science and Engineering, Babeș-Bolyai University, for the technical support given in this research.

REFERENCES

Abhilash P.C., Singh N., 2009, Pesticide use and application: an Indian scenario. *Journal of Hazardous Materials*, **165**, pp. 1-12.

Afful S., Anim A., Serfor-Armah Y., 2010, Spectrum of organochlorine pesticide residues in fish samples from the Densu Basin. *Research* Journal of *Environmental* and *Earth* Sciences, **2** (3), pp. 133-138.

Aiyesanmi A.F., Idowu G.A., 2012, Organochlorine pesticides residues in soil of cocoa farms in Ondo State Central District, Nigeria. *Environment and Natural Resources Research*, **2** (2), pp. 65-73.

Belta G.D., Likata P., Bruzzese A,, Naccarri C., Trombetta D., Turco V.L., Dugo C., Richetti A,, Naccari F., 2006, Level and congener pattern of PCBs and OCPs residues in bue-fin tuna (*Thunnus thynnus*) from the straits of Messina (*Sicily, Italy). Environmental Intternational*, **32**, pp. 705-710.

Dai J.Y., Chen L., Zhao J.F., Ma N., 2006, Characteristics of sewage sludge and distribution of heavy metal in plants with amendment of sewage sludge. *Journal of Environmental Sciences*, **18** (6), pp. 1094-1100.

Ene A., Bogdevich O., Sion A., 2012, Levels and distribution of organochlorine pesticides (OCPs) and polycyclic aromatic hydrocarbons (PAHs) in topsoils from SE Romania. *Science of the Total Environment*, **439**, pp. 76-86.

Megharaj M., 2002, Heavy pesticide use lowers the soil health. *Farming Ahead*, **121**, pp 37–38.

Official Monitor of Romania. Reference values for traces of chemical elements in soils. O.M. No. 756/03.11.1997: Monitorul Oficial al Romaniei (Partea I, No. 303 bis/1997); 1997 (in Romanian).

Raposo Jr. L.J., Re-Poppi N., 2007, Determination of organochlorine pesticides in ground water samples using solid-phase microextraction by gas chromatographyelectron capture detection. *Talanta*, **72**, pp. 1833-1841.

William J., Tagoe L., Drechsel P., Kelderman P., Gijzen H., Nyarko E., 2008, Accumulation of persistence organochlorine contaminants in milk and serum of farmers from Ghana. *Environmental Research*, **106**, pp. 17-26.

Yadav I.C., Devi N.L., Syed J.H., Cheng Z., Li J., Zhang G., Jones K.C., 2015, Current status of persistent organic pesticides residues in air, water, and soil, and their possible effect on neighboring countries: A comprehensive review of India. *Science of the Total Environment*, **511**, pp. 123-137.

Zhang W.J., Jiang F.B., Ou J.F., 2011, Global pesticide consumption and pollution: with China as a focus. *Proceeding of the International Academy of Ecology and Environmental Science*, **1** (2), pp. 125-144.